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March 6, 1967
DMIC Memorandum 228

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ACCELERATED CRACK PROPAGATION OF
TITANIUM BY METHANOL, HALOGENATED
HYDROCARBONS, AND OTHER SOLUTIONS

DEFENSE METALS INFORMATION CENTER
BATTELLE MEMORIAL INSTITUTE
COLUMBUS, OHIO 43201

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ACCELERATED CRACK PROPAGATION OF TITANIUM BY
METHANOL, HALOGENATED HYDROCARBONS,
AND OTHER SOLUTIONS

INTRODUCTION

The failure in late 1966 of a titanium-alloy tank by methanol stress-corrosion cracking resulted in a flurry of activity to investigate the behavior of titanium and its alloys in various media such as the alcohols and fluorinated hydrocarbons. The Defense Metals Information Center sponsored a seminar on this subject in cooperation with NASA Manned Spacecraft Center. The seminar on "Accelerated Crack Propagation of Titanium by Methanol, Halogenated Hydrocarbons, and Other Solutions," was held at Battelle Memorial Institute in Columbus, Ohio, on March 6, 1967. This was attended by 139 persons representing 78 individual companies and offices of the US government.

Technical presentations were solicited from those researchers working on the subject. Because of the short notice given for this meeting, no formal manuscripts were prepared in advance. However, to make the results of this program more widely available, all presentations were tape recorded, and a transcript of each talk was prepared. After editing and review by the speakers, these presentations were gathered together to form the present memorandum. In addition, one paper from The Marquardt Corporation was later submitted to DMIC and is included as an appendix to this memorandum.

Mr. James D. Jackson, Research Chemical Engineer in Battelle-Columbus Corrosion Research Division organized the seminar and was chairman of the sessions. Mr. Walter K. Boyd, Chief of the Corrosion Research Division, was host and led the discussion and summation of the program. Mr. Daniel J. Maykuth, Assistant Director of the Defense Metals Information Center, was in charge of the arrangements.

DMIC also gratefully acknowledges the contributions of all of those who participated in the program and to their parent companies and organizations for permission to reproduce these results from that meeting.

NASA EXPERIENCES WITH Ti-6Al-4V IN METHANOL

by
 R. E. Johnson
 NASA Manned Spacecraft Center
 Houston, Texas

This paper describes the results of two different types of work that have been conducted in recent months. The first is a rather straightforward engineering-type program that was run in house at Manned Spacecraft Center (MSC) in Houston. The second effort involved a fracture mechanics-type of investigation that was conducted under contract to Messrs. C. Tiffany and J. Masters at the Boeing Company in Seattle, Washington. To describe this work, it is necessary to review some of the Apollo tanks that have been under test, and show the sources of test material used in the work.

The test material essentially came from three sources. MSC had two tanks that were available from test, and some sheet material was furnished to MSC by the Titanium Metals Corporation of America. This material was Ti-6Al-4V furnished to us in the solution-treated-and-aged (STA) condition. The locations of the test material from the two tanks are shown in Figures 1 and 2.

Figure 1 illustrates a tank that failed while under test at North American, Downey, California. This tank was being pressure tested with dry, reagent-grade methanol, which is used as a referee fluid in place of the fuel that is intended for ultimate use. During the testing, which was a sustained-pressure test, it was noted that a leak developed in the heat-affected zone of the lower weld.

For information, this tank is about 14 feet in length and the diameter is approximately 51 inches. The wall thickness is about 0.060 inch and the weld land thickness is about 0.070 inch. Note the location of the failure in relation to the test material that was used in the program at MSC in Houston. Near the lower end of the tank, three small cracks opened up in the heat-affected zone of the weld and permitted the methanol to leak out. The test material was taken from the opposite side, 180 degrees from this location, and included both parent and weld material. The second tank, Figure 2, is referred to as Spacecraft 17 material. This tank failed catastrophically in test, also with methanol as the pressurant. The origin of failure was not associated with the weld zone, but was found to be some 10 inches above the weld land in the parent material. It can be seen in Figure 2 that the test material was taken from the middle portion of the tank, in an area well removed from the fractured area. The test material again included both parent and weld metal.

Various types of tests were performed at the Center, including fatigue tests as well as sustained-load tests. For those interested in microstructural effects, the mode of fracture was both transgranular and intergranular. From fractographs which were prepared, it was obvious that ductile shear failure occurred away from the origin of failure, but

fracture facets observed in the origin of failure are considered to be typical of stress-corrosion cracking.

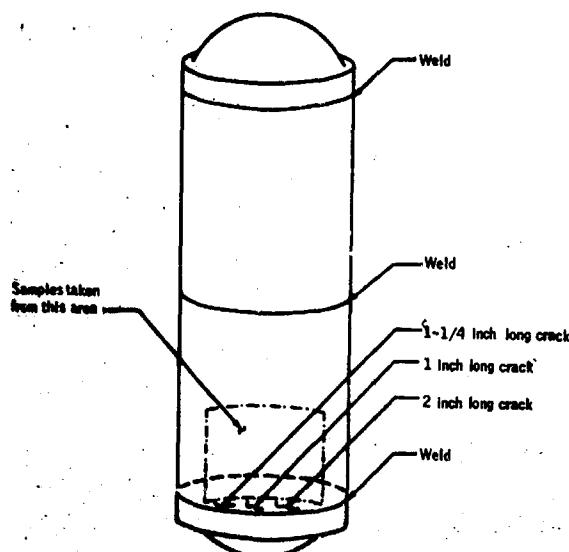


FIGURE 1. APOLLO S/C 101 PRESSURE VESSEL

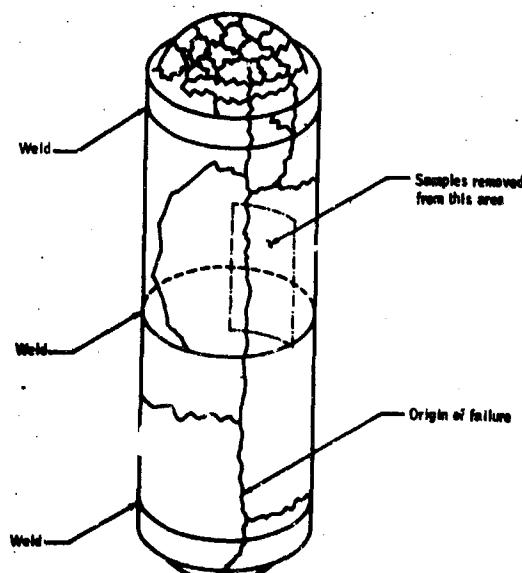


FIGURE 2. APOLLO S/C 017 PRESSURE VESSEL

The specimen configuration used at MSC is shown in Figure 3. The specimen is a standard ASTM specimen and is mounted in a glass tube, sealed at the bottom with a cork or rubber stopper. In some cases, it was necessary to seal with paraffin wax around the base of the container to prevent loss of the methanol during testing. The glass tube was filled with the fluid that was under test in contact with the titanium alloy. In the case of methanol and some of the other fluids, it was found that the hygroscopic nature of the fluid required sealing of the top of the tube as well. For all of the test data presented on methanol, the tests were performed using a plastic sheet wrapped completely around the glass tube to prevent water pickup from the atmosphere.

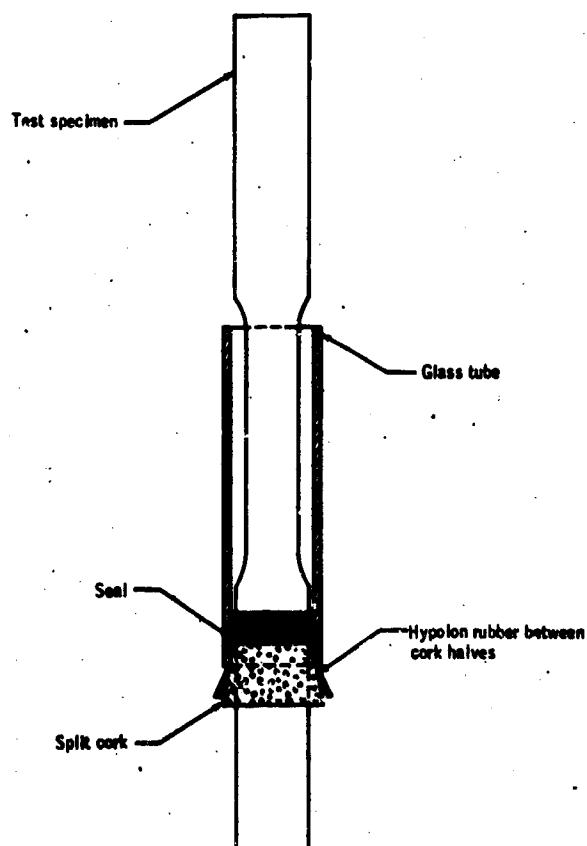


FIGURE 3. TEST SPECIMEN IN FLUID CUP

Notched specimens were also tested; configuration is shown in Figure 4. As indicated, these contained a 60-degree V-notch with a root radius of 0.003 inch. In addition, a rather unusual test specimen was used that had double (or two) reduced test sections. The idea was to examine the material that had been exposed to methanol and then to test it in some other environment. In order to do this, both test sections were immersed in the fluid until failure occurred in one of the test sections. The specimen was then cut in half to remove the failed portion, and the second specimen, which had seen the identical exposure but had not failed, was then tested in a different environment.

No attempt is made in this paper to present the fatigue data that were gathered from these tests. These data are available in NASA TN D-3868, entitled "Stress Corrosion Cracking of Ti-6Al-4V in Methanol", printed in February, 1967. In general, however, these tests showed that methyl alcohol did lower the fatigue capability of the Ti-6Al-4V alloy over that in other fluids as well as in air.

Table 1 shows some of the sustained-load-test results with various test materials. In looking at the specimens from the tanks, it was found that fairly short time periods were required to fail the material at moderate stresses. In contrast, the virgin sheet material, which had no prior exposure to any other fluid, required a considerably longer time-to-failure than the materials from the tanks. Part of this difference could have been due to the fact that the materials from the tanks had seen other fluids. However, another possible effect was considered since the tanks had a blue oxide on their interior surfaces as a result of stress relieving the material in air at approximately 1000 F. In looking at this type of failure in the tank material it was questioned whether the oxide was contributing to the rapid failure, so a few tests were run to find the extent of this effect. The first two data points in Table I show that there is an apparent effect. These data have been verified with other work to show that there is an effect in methyl alcohol of the surface condition on the material. For example, virgin sheet material, unnotched at 140 ksi, went longer than 300 minutes without failure in methyl alcohol. The same material, aged 4 hours at 1000 F in air before testing, failed in an average of 63 minutes.

It can be seen from Table 1 that other fluids were also tested. In one case involving virgin material in ethylene glycol plus water, there was no failure in over 3000 minutes. Similarly, tests in water with 500 ppm of sodium chromate inhibitor again showed no failure in fairly long time periods. It is noted that these tests were at fairly high stresses, and in this case, the specimens were notched.

It was noted that samples tested in methyl alcohol at 120 ksi failed in 144 minutes; samples tested in ethylene glycol and water again showed no failure. Another specimen, tested in isopropyl alcohol, survived more than 3000 minutes without failure at 140 ksi.

No failures were observed on samples tested in Aerozene 50 or in distilled water.

In summary, the work that was done in house showed that the only fluid that caused rapid failure of Ti-6Al-4V alloy was dry methyl alcohol.

A brief summary of the work that was sponsored by MSC at the Boeing Company follows. This work was recently completed and the final report is available as NASA CR-65586.

TABLE I. CONSTANT LOAD DATA^(a)

Specimen Origin	Number of Specimens	Notched	Load, ksi	Test Fluid	Time to Failure, min	Standard Deviation, min	Remarks
Virgin	1	No	140	Methanol	>300	-	
Virgin	2	No	140	Methanol	63	3	Aged additional 4 hours at 1000 F in air before testing
Virgin	4	Yes	120	Methanol	31	16	
Virgin	5	Yes	120	Ethylene glycol/H ₂ O	>3183	-	No failures
Virgin	4	Yes	120	H ₂ O/sodium chromate	>2880	-	No failures
Virgin	2	Yes	120	Methanol	44	28	Aged 30 minutes at 1000 F before testing
Virgin	1	Yes	130	Methanol	20	-	
Virgin	5	Yes	140	Methanol	19	5	
Virgin	8	Yes	140	Ethylene glycol/H ₂ O	>3588	-	No failures
Virgin	1	Yes	140	Isopropyl alcohol	>3042	-	No failures
SC 017 ^(b)	5	No	90	Methanol	28	10	
SC 017	4	No	100	Methanol	33	5	
SC 017	4	No	120	Methanol	12	1	
SC 017	1	No	120	H ₂ O sodium chromate	>2880	-	No failures
SC 017	5	No	140	Methanol	7	1	
SC 101 ^(b)	5	No	90	Methanol	24	4	
SC 101	5	No	100	Methanol	24	10	
SC 101	10	No	120	Methanol	17	22	
SC 101	2	No	120	Air	>4463	-	No failures
SC 101	1	No	130	Methanol	2	-	
SC 101	5	No	140	Methanol	6	1	
SC 101	3	Yes	120	Methanol	9	2	
SC 101	3	Yes	120	Aerozine-50	-	-	Specimens loaded for over 2 weeks with no failure at this writing
SC 101	2	Yes	120	Distilled H ₂ O	>2565	-	No failures

(a) Several specimens were exposed to methanol without failure for extended periods of time at stresses below 100 ksi. However, the methanol, due to its hygroscopic properties, was diluted with water to various amounts which undoubtedly influenced the time-to-failure. These specimen results were not included in the above table.

(b) Spacecraft.

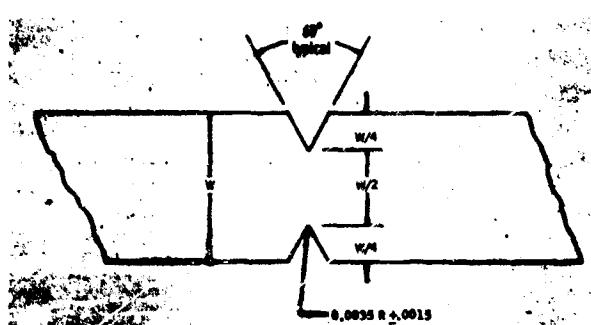


FIGURE 4. NOTCH CONFIGURATION USED AT NASA-MSC

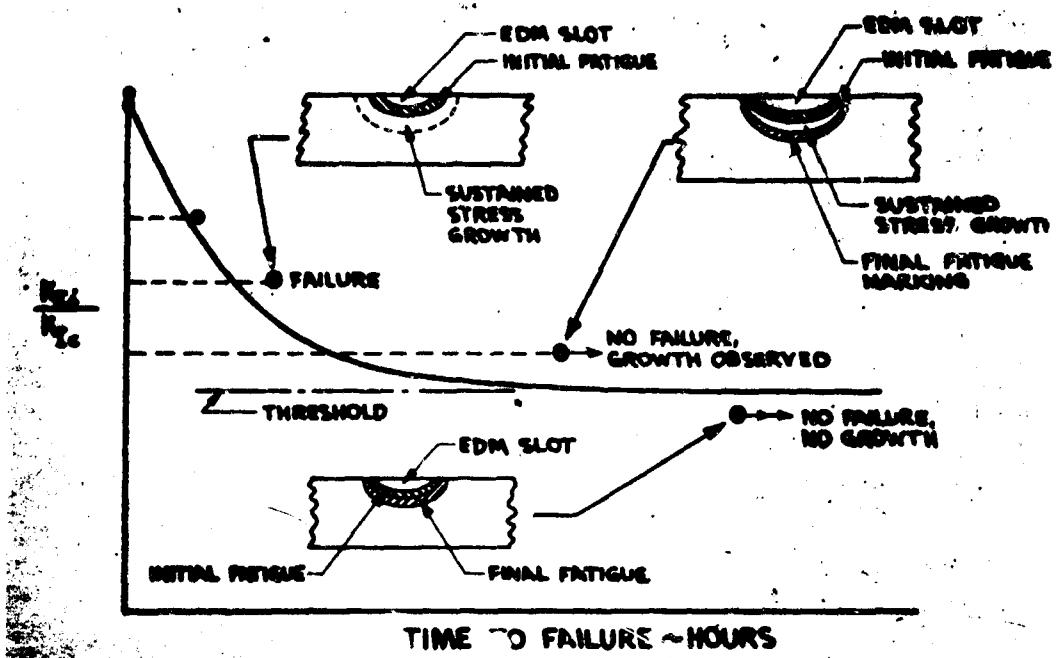


FIGURE 5. EXPERIMENTAL APPROACH FOR SUSTAINED-STRESS FLAW-GROWTH TESTS

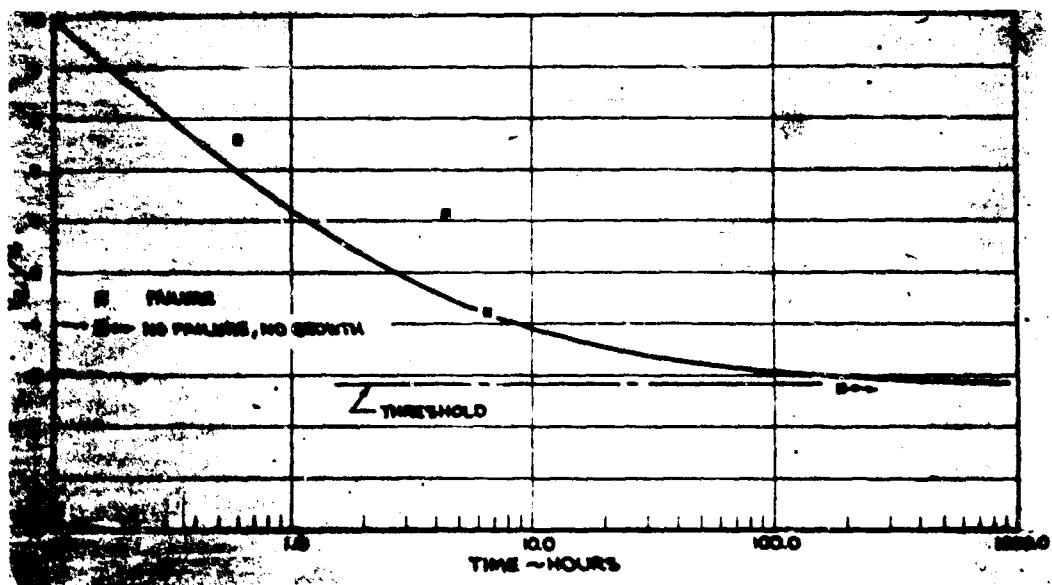


FIGURE 6. SUSTAINED-STRESS FLAW-GROWTH DATA OF 6Al-4V TITANIUM WELDMENT H.A.Z.
IN METHANOL AT ROOM TEMPERATURE

The specimens used were machined and pre-cracked in fatigue. MSC furnished Boeing material from new cylinders that are used to make the tanks that were described earlier. This material was made and processed the same way as the failed tanks but did not see the history of methanol exposure. Otherwise, this material had gone through all of the other processing steps that the failed tanks had seen. Weldments as well as parent material were included. The parent material was taken in a circumferential direction so a bending moment correction to the stress level was necessary.

The experimental approach used is probably familiar to most. The approach utilizes a partial through-crack test. The objective was to determine the conditions of stress and flaw depth where crack growth was observed in some relatively short period of time. In order to do this, the specimens were first machined by electrodischarge machining to give a flaw starter. Then, a fatigue precrack was introduced into the specimen. The depth of the fatigue crack could be controlled and varied by the conditions of the fatigue test. This type of specimen was then put into the test environment and stressed. Within a period of time, either failure did or did not occur. In the case of failure, the fracture looked something like that illustrated in Figure 5. If failure did not occur, the specimen was taken out of the test, refatigued in order to mark it, and then tested in tension. In this case, there were two possible results; observable crack growth or no observable crack growth as illustrated in Figure 5. The results of numerous tests were then plotted on a curve of the type shown in Figure 5. By this approach and introducing various combinations of stresses and flaws in the materials, a curve such as that shown in Figure 5 was developed. This gave a percent of K_{Ic} as a threshold value for a specified time for each fluid. The Boeing investigators did this with many fluids for MSC; Figure 6 is an illustration of the type of curve that was found in methyl alcohol. You can see that the threshold is fairly low, on the order of 28 percent of K_{Ic} at room temperature using reagent-grade methanol.

The K_{Ic} values averaged about 44 ksi $\sqrt{\text{in.}}$ for the weldments at room temperature, the precrack was introduced at the heat-affected zone of the weld. To illustrate the contrast in thresholds, note from Figure 7 that the threshold observed in Aerozene 50 at room temperature is over 80 percent of K_{Ic} ; also seen is that with an increase in test temperature the threshold has been reduced.

Figure 7 also shows how these data can be used. The curve on the right is the K_{Ic} curve which represents the condition of flaw depth and stress that will give failure in a tensile test. The other curves are threshold curves. To insure against slow crack growth, one would want to operate to the left of the curve for the fluid under consideration. For example, in Figure 7, note the relative positions of the curves for Aerozene 50, methyl alcohol, and the effect of temperature. These data help to explain the Apollo tank failures that occurred. You will note that even at fairly low stresses a

fairly shallow flaw will start to grow in methyl alcohol. Also, even though it has to grow to the K_{Ic} curve before failure occurs, the time involved is very short.

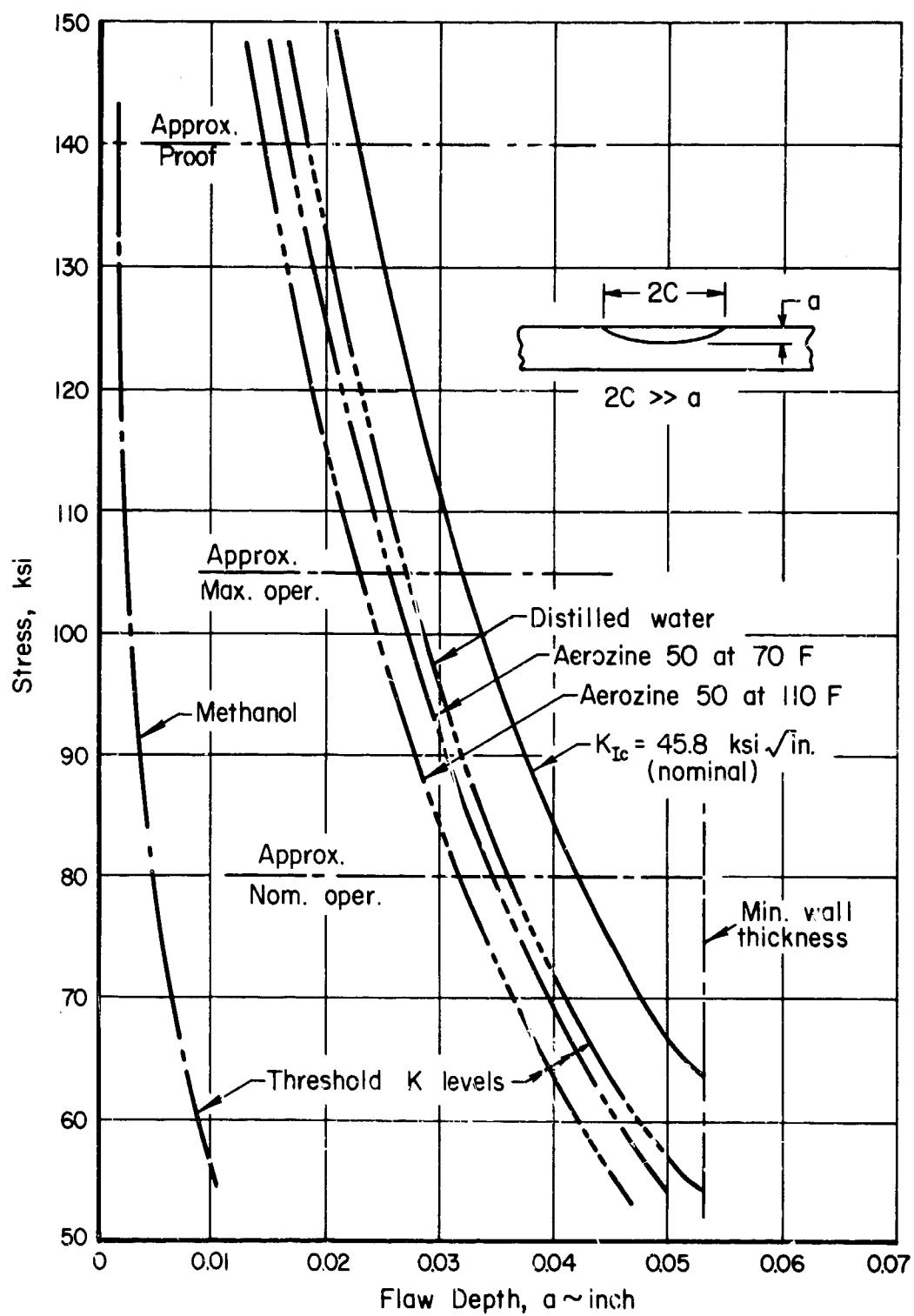


FIGURE 7. CRITICAL & THRESHOLD FLAW SIZE CURVES

**PREMATURE ENVIRONMENTAL STRESS CRACKING OF
TITANIUM IN METHANOL, FREON, AND OTHER SOLUTIONS**

Robert O'Brien
North American Aviation Incorporated
Downey, California

My purpose in being here today is not to burden you with details of tank failures but rather to bring you a message. It is a message that we at North American have learned and are now practicing, and I hope that it will be a benefit to you.

In the way of introduction, let me tell you a little about the work we have done. We have had essentially three problem areas with Apollo titanium tanks:

- (1) Premature failure of tanks containing N_2O_4 , with which most of you are probably now familiar
- (2) A similar type failure with the use of methanol
- (3) Accelerated crack propagation of a Ti-6Al-4V tank containing Freon MF.

One might ask why and where these fluids are being used. N_2O_4 , of course, is used because of its high specific impulse. It is intended for use in a reaction control system and a service propulsion system oxidizing tank.

Methanol is used, because of its fluid dynamic characteristics, to simulate the fuel in cold flow system tests. Methanol has also been used by a number of contractors in various cleaning activities.

Freon MF fits pretty much in the same category as methanol. It is used for fluid dynamic considerations in the testing of SPS oxidizer tanks and cold flow system tanks, and in some cleaning operations.

In reviewing the literature and knowledge of these current problem areas, we at North American ran a series of stress-corrosion tests in nitrogen tetroxide in early 1962 and did not experience any problems. This involved about 27 specimens that were tested at ambient temperature. As far as methanol is concerned, our knowledge from the literature was that methanol containing hydrogen chloride could be damaging. We knew of no work that had been done using methanol of reagent grade or conforming to methanol of Federal Specification OM-232d. To our knowledge, there were no problems reported with the use of Freon MF.

Now briefly, what are our findings for these three fluids? Stressed Ti-6Al-4V tanks failed with N_2O_4 exposure in as little as 30

hours. These failures were proved to result from stress corrosion of the Ti-6Al-4V alloy, and the simple addition of NO to the N_2O_4 inhibited and stopped the corrosive attack. In the case of methanol, we have had tank failures of stressed Ti-6Al-4V in as little as three hours. Laboratory tests confirmed the incompatibility between the stressed Ti-6Al-4V and the anhydrous, that is, dry, spec-grade methanol. A 1 percent water addition to the methanol inhibited the attack. However, methanol with 1% water and as low as 5 ppm or 15 ppm of chloride ion did not prevent failure. Apollo tank material from two failed tanks did not fail in laboratory tests at NAA when exposed to Freon MF at stress levels up to 130 ksi. We did have two failures, however, of Ti-6Al-4V specimens from contaminated sheet weld material, which we prepared purposely to test the effect of defective welds. In both cases, the failure occurred in the defective welds at a stress of 120 ksi.

We have, in our Apollo program, developed a test specimen that we use to determine whether an environmental-stress-cracking condition may exist. This we refer to as a miniature notched specimen. It is about 3 inches long, 0.5 inch in diameter, and has a root radius of 0.001 inch at the base of the notch.

I will now briefly describe, in chronological order, some of the test results obtained at NAA on these three problem areas.

We tested a total of 464 specimens in N_2O_4 , of which we were able to secure failure of 84. These specimens were tested at either room temperature or 165 F and at imposed stress levels of 30 to 135 ksi. These included 311 unnotched sustained-load type specimens, 20 notched sustained-load type, and 133 bend-test samples. The nitrogen tetroxide used was from our bulk storage cylinders, which came directly from the manufacturer and conformed to the Mil-P-26539A grade. To this grade of N_2O_4 , we added various additives and/or contaminants. We also used a grade of N_2O_4 which has come to be known as NASA Spec-Grade MSC-PPD-2 and which contains an excess of NO. The Ti-6Al-4V material used was in the STA condition. Some of this was material salvaged from the original failed Apollo tanks while additional samples were prepared from newly purchased and heat-treated sheet. We refer to this latter as referee sheet material. The parameters evaluated in the N_2O_4 test program included many variables of the manufacturing processes including, for example, cleaning prior

to welding and/or heat treatment, metallic coupling, various contaminants and inhibitors in the N_2O_4 , effects of oxidation and heat-treating oxide scale, and the use of anodizing and/or shot peening treatments on the surface of the Ti-6Al-4V tanks.

In our work with methanol, we have completed testing of 236 specimens and further tests are in process. Of 236 tests completed, we have failed 163 of the coupons. Here, we have imposed stress levels of 30 to 125 ksi. The time to failure has varied quite a bit, ranging from as little as 2-1/2 hours to perhaps 15 days as a maximum period. Again, the material being tested represents both the Apollo tank material as well as referee sheet material of 0.020- and 0.080-inch thicknesses. On this test program, we have included 191 notched sustained-load type specimens, 12 unnotched sustained-load type specimens, and 33 bend test specimens. Some of the methanol used has been from our North American bulk storage, but the majority of our specimens have been tested in reagent-grade methanol. We have also tested some samples in methanol vapors. The parameters evaluated in this test program have included cleaning, stress relieving after machining and after welding, bimetallic coupling, the addition of water, and the addition of chloride ions.

Lastly, on our work with Freon MF, we have prepared 170 laboratory test specimens of which 7 have failed. Five of these samples were exposed in a one-to-one-mix of methanol and Freon MF, and 4 of these 5 specimens did fail. We also ran 4 specimens in a one-to-one mix of methanol and Freon MF vapors, and 1 of these 4 specimens also failed. Essentially, our findings are somewhat different than those obtained at NASA NSC in that we have not experienced failure of either tank material or referee sheet material in Freon MF. Test temperatures again have been room temperature and 115 F at imposed stress levels of 80 to 130 ksi. The time to failure, where we did have the methanol mixed with Freon MF, has been as little as 2.1 hours. Our maximum failure time on the 7 specimens cited was 12 hours. Again the material tested represents Apollo Ti-6Al-4V tank material as well as referee Ti-6Al-4V sheet material of 0.030- and 0.080-inch thicknesses. The samples tested to date have included 142 notched sustained-load specimens, 15 unnotched sustained-load specimens, and 4 bend-test specimens.

During the course of evaluating Freon MF, we also embarked upon an effort to take a look at a lot of other fluids that titanium could see in various processing stages by our various contractors and subcontractors. Specifically, we are looking at cleaning and tank-manufacturing practices, and the effects of welds and of selected contaminants and inhibitors. We have had tests performed in Freon TF, Aerozene 50, distilled water, and distilled water with sodium chromate additions. We have also tested in trichlorethylene, benzene, monomethyl hydrazine, and other solvents with HCl additions, and in air. In none

of these cases have we had any failures of Ti-6Al-4V.

At North American, we use the term environmental stress cracking rather than the term stress corrosion, simply because the classic corrosion products, as we think of them, may not always be present or evident in the fracture faces of the failed specimens. We know that the role of the chloride ion is important and, under some conditions permitted by some specifications, a trace of this ion may prove disastrous. The mechanism of failure of titanium by various fluids affords a broad area of endeavor. However, project considerations often require a quick fix, and we in projects of this sort must direct our efforts toward obtaining the quick fix in order to use hardware that has been made and is now available. Our experiences also indicate that there is a stress threshold below which failures do not occur. However, this level is so low for STA Ti-6Al-4V that it is not useful for the Apollo mission requirements.

I feel that for a project such as the development of the supersonic transport, where there could be dozens, if not hundreds, of small fabricating shops hot forming titanium, that it is absolutely imperative that the quality control function be tightened to reduce the possibility of subsequent environmental-stress-cracking failures. At North American's Space and Information Division, we have detailed all the environmental fluids that the titanium "sees from the cradle to the grave". We have in-house specifications that govern what can and cannot be used, and I would certainly strongly recommend this approach for the supersonic transport as well as any other aerospace programs.

EFFECTS OF SOME ORGANICS ON THE STRESS
CORROSION SUSCEPTIBILITY OF SOME TITANIUM ALLOYS

by

Dr. George Sandoz
U. S. Naval Research Laboratory
Washington, D. C.

Gentlemen, I want to tell you about our work at the Naval Research Laboratory on the effects of a number of the organics on titanium alloys. Our interest in this has been primarily from the service difficulties that we have heard about. We had in the past examined some pre-cracked titanium specimens in such things as carbon tetrachloride, benzene, and methanol, and we found that they would crack. However, our chemist gave us such a hard time on purity that we sort of dropped the subject. We have now renewed our interest and have run a number of tests. The results are still tentative. While we may have to change our minds on some of these, we think they give a good deal of circumstantial evidence on the mechanisms involved and this is really what we are looking for -- to get some idea about the mechanisms and not simply to find out every environment that will crack titanium.

We have run two types of tests on the alloys. The alloys that we have used are the Ti-8Al-1Mo-1V and the Ti-6Al-4V alloys. We have run tests using unnotched specimens and precracked specimens. Results from each type were related to the initiation of fracture from stress corrosion and to propagation. The test I will describe employed a cantilever beam with which I think most of you are familiar. A rectangular specimen containing a fatigue crack is used. An environment is placed around the specimen by means of a flexible bag. If the specimen has a fatigue crack, you can interpret your results with fracture mechanisms giving K values. When specimens are run dry and in the environment, it is possible to get a feeling for the degradation that occurs, and you can determine the threshold K values. If it is unnotched, an estimate of the stress at the surface may be obtained from the old formula

$$S = \frac{NC}{I}$$

where

S = stress at the surface

N = bending moment about the neutral axis

C = distance from neutral axis

I = moment of inertia about the neutral axis.

I will first review the test results on unnotched specimens where, essentially, we are evaluating crack initiation. Then, I will go through the series of slides showing the results on the precracked specimens, and finally I will speculate on what this tells us about the mechanism.

Table 1 summarizes our data for the unnotched or smooth specimens. Our environments have included methanol, ethanol, propanol, normal hexane, and ethylene glycol. We have two lots of the alloy, Ti-8Al-1Mo-1V with yield strengths of 135 and 123 ksi, and one lot of Ti-6Al-4V with a yield strength of 135 ksi. The numbers beside the data points indicate the stress, in ksi, on our specimen, and the second number tells us the time of the test. The letters above indicate whether the specimens broke or did not break. We got cracks in methanol, but we did not get a crack in ethyl alcohol. However, this turned out to be wrong. One specimen did break after about 300 hours, so you can crack a specimen in ethyl alcohol. We were not able to crack specimens in normal propanol in the times indicated nor in normal hexane in 69 hours. We were able to crack the Ti-8Al-1Mo-1V alloy using ethylene glycol. We were not able to crack the Ti-6Al-4V alloy in ethylene glycol.

In the other tests indicated here, we have sodium chloride, water, and glycerin added to methanol. I will simply say that the sodium chloride accelerates the cracking to give cracking in a shorter time. The glycerine or water slows it or maybe completely retards it, as compared to methanol itself. So, we have shown that we can initiate cracks in methanol, ethanol, and ethylene glycol, but apparently not in the longer chain alcohols and not in the straight-chain hydrocarbons.

In the tests using the precracked specimens, the dry fracture (K_I) toughness values are around 80-90 ksi $\sqrt{\text{in}}$. In the environment that we show in Figure 1, we come down to a threshold value of 23 ksi $\sqrt{\text{in}}$. In other words, the cracks are propagated at these stress intensity levels. Below these stress intensity levels, the cracks do not propagate. Figure 1 shows results with pure methanol, methanol plus salt and water, and salt water. I know we do not want to consider salt water, but a brief comparison with methanol shows the salt water curve is at about the same level. These curves are included to indicate that methanol plus salt plus a precrack produces a fracture in a short time with 2 percent water in the solution, whereas we could not start cracks with the 2 percent water present.

Figure 2 illustrates the ethylene glycol curve. We actually have tested one specimen, step loaded as shown, and two other specimens. On this figure, a little number marked with an arrow indicates that a single specimen was step loaded. All of these curves will show a break in the curve, the scale here going to longer times. As you can see, in ethylene glycol, there

TABLE I. SMOOTH SPECIMEN TESTS IN ORGANIC LIQUIDS

Alloy	Environment(a)					
	Methanol + NaCl + 2% H ₂ O	Methanol	Abs. Ethyl Alcohol + 1% Glycerine	n-Propyl Alcohol	n-Hexane	Ethylene Glycol
Ti-8Al-1Mo-1V (135 YS)	B (160, 3 min)	NB (116, 83 min)	(99, 20 hr)	(99, 0.7 hr)	NB (123, 69 hr)	
	B (145, 7 min)			NB (107, 26 hr)		
	B (116, 45 min)			NB (115, 1.5 hr)		
Ti-8Al-1Mo-1V (123 YS)			NB (67, 2.7 hr)		NB (100, ~30 hr)	B (>YS, 1 min)
			NB (125, 160 hr)			
Ti-6Al-4V (135 YS)	B (weld) (74, 2.3 hr)	NB (70, 6 hr)	(109, 1 hr)			B (99, 1.9 hr)
	B (base) (100, 2.4 hr)	B (83, 3 hr)				NB (104, 6 hr)
		NB (67, 1.5 hr)				NB (114, 19 hr)
		B (79, 1.5 hr)				NB (123, 3 hr)
		B (109, 37 hr)				NB (138, 24 hr)
			B (138, <5 hr)			B (138, 10 hr)

(a) B and NB designate samples which broke or did not break, respectively, in the exposures indicated. Values in parenthesis give stress level (ksi) and exposure time (in hours).

is a degradation of K_I to about the same level as in the water.

Figure 3 shows our results with ethyl alcohol, a similar type of curve. In this case, we got a little higher K_I threshold level, somewhere around 34 ksi $\sqrt{\text{in.}}$

Figure 4 gives our data for normal butanol. Again, a somewhat similar type curve results, coming down somewhat slower than the water curve but coming in about 30 ksi $\sqrt{\text{in.}}$

Figure 5 shows results obtained in a longer straight chain alcohol, decanol. Note that here we have a break in 12 hours at a value around 40 ksi $\sqrt{\text{in.}}$

Figure 6 shows results with a tertiary butyl alcohol. Of the data points here, one was obtained with an impure grade and the others with a much purer grade of the same alcohol. So we feel purity is not too vital in this case.

Figure 7 gives results on a test that we ran on propane, which is a straight-chain hydrocarbon gas. Sure enough we got degradation, but we only had one specimen on this.

Figure 8 illustrates a curve obtained in normal hexane. Here, we have enough data to pretty well establish that there is a degradation of K_I here to about 40 ksi $\sqrt{\text{in.}}$

Figure 9 shows a curve for heptane. These data are also limited, but we do have these points to indicate that the K_I value is at about the same level, that is, 35 to 40 ksi $\sqrt{\text{in.}}$

Figure 10 shows some data we obtained with the Ti-6Al-4V alloy that we tested in salt water. Here, we found the K_I , K_x , or K_c

values are the same. Thus, we get a value of about 62 ksi $\sqrt{\text{in.}}$ in tests up to 200 hours. We took the same material tested in methanol, and within 5 minutes, we could get a break with a K value around 50 ksi $\sqrt{\text{in.}}$ So there you have a case where a specimen will not crack in water, but will crack in methanol with a precrack present.

You will recall that with the other alloy (Ti-8Al-1Mo-IV) the K_I values in water and

methanol were almost identical. There are possible reasons for this. One is that the Ti-6Al-4V specimens for some reason tend to creep very rapidly, which may be playing a part in where our K_I comes. Also, we may be getting blunting of the crack before a reaction can take place, which would cause the cracking to propagate. This, conceivably, could lower the stress.

Table 2 summarizes the values that we got in our stress-corrosion cracking index for the Ti-8Al-1Mo-IV alloy. Remember the dry fracture

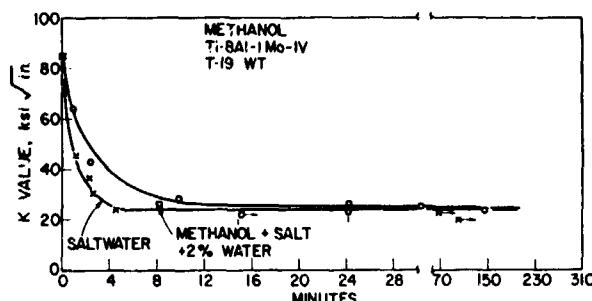


FIGURE 1

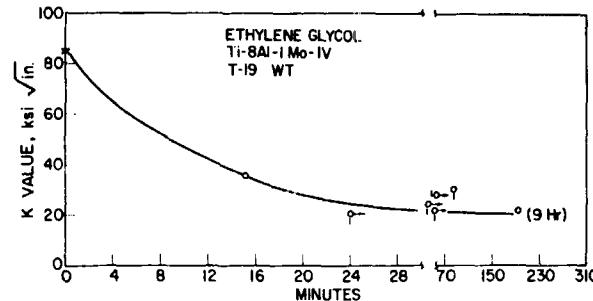


FIGURE 2

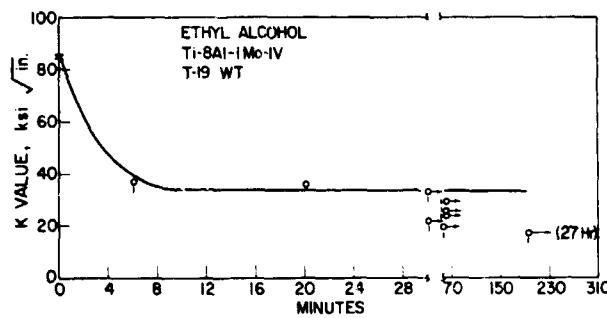


FIGURE 3

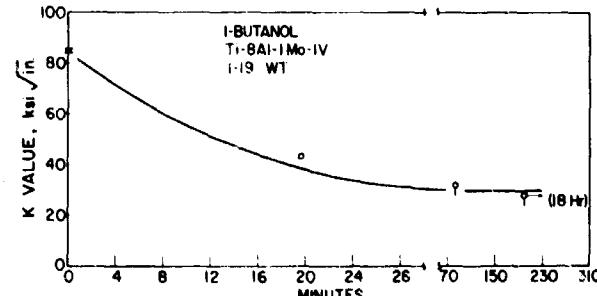


FIGURE 4

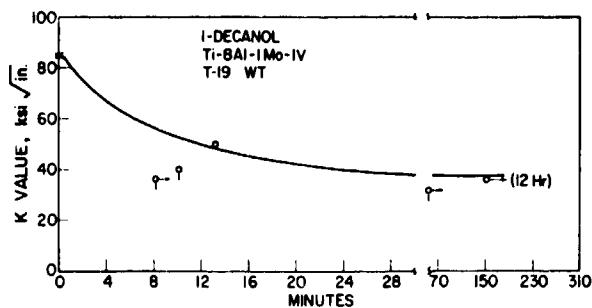


FIGURE 5

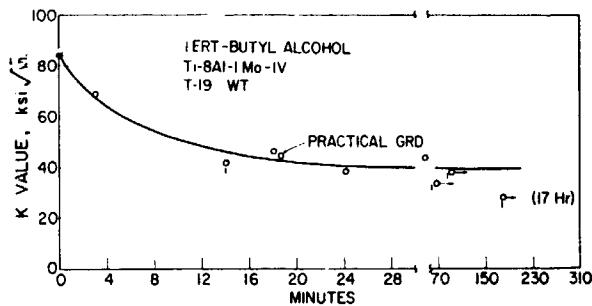


FIGURE 6

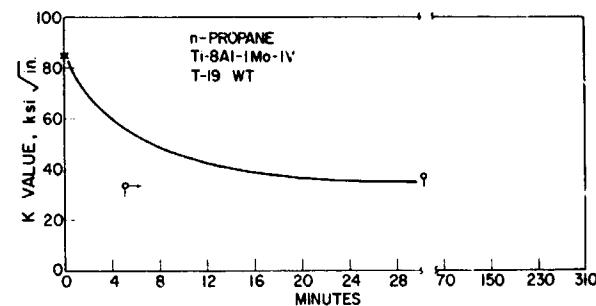


FIGURE 7

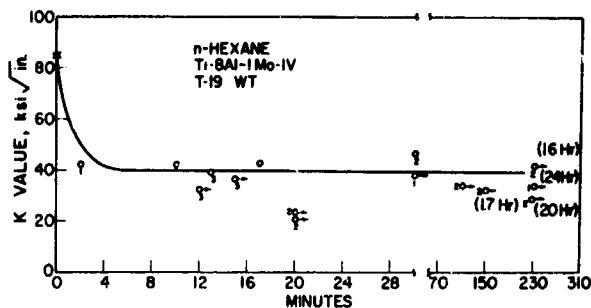


FIGURE 8

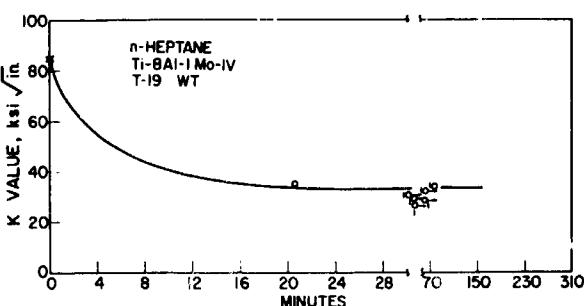


FIGURE 9

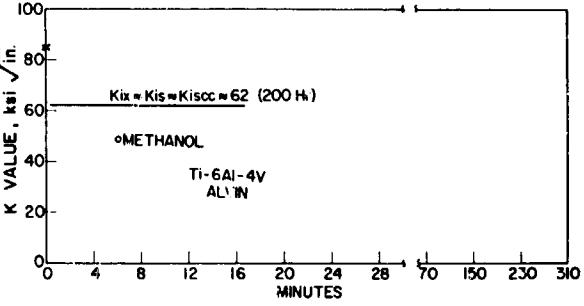


FIGURE 10

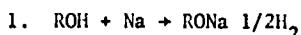
toughness on this alloy runs about 85 ksi $\sqrt{\text{in.}}$. In ethylene glycol, methanol, and ethyl alcohol, the $K_{I_{\text{sc}}}$ values are rather low, the same as in

salt water. Then, there is a gradual trend upwards in $K_{I_{\text{sc}}}$ values to about 38 ksi $\sqrt{\text{in.}}$ as

you get to the longer chain alcohols. Notice that the normal alcohols, propanol and butanol, compared to the secondary and tertiary alcohols, tend to give lower $K_{I_{\text{sc}}}$ values.

I have a little more to add on this because of a reaction that I am proposing. This is shown below for two reactions which I have tentatively proposed as perhaps explaining data that I have obtained.

POSSIBLE REACTIONS



2. CRACKING

EVIDENCE ON REACTION 1

A. Smooth Specimens

1. Favor

- a. Crack methyl, ethyl, ethylene glycol

- b. Small amount water, glycerine slows
- c. Methanol and n-hexane do not crack steels
- d. n-hexane does not crack titanium

2. Oppose

- a. Water does not start crack
- b. Long-chain primary alcohols may not start cracks

B. Precracked Specimens

1. Favor

- a. Tertiary alcohol gives higher K_I_{SCC}
- b. Methanol and n-hexane do not crack steel

2. Oppose

- a. Even tertiary alcohol give low K_I_{SCC}
- b. In Ti-6Al-4V alloy, water does not propagate crack
- c. Straight-chain hydrocarbons do propagate cracks

I would like to give you these items and let you judge for yourself. In organic chemistry, we see examples of Reaction 1 listed in every textbook in which an alcohol reacts with an active metal, such as sodium, to form an alkoxide plus hydrogen gas. Other metals besides sodium, including magnesium and aluminum, have been mentioned as entering into this type of reaction. I have not heard anybody mention titanium as also possibly entering into this reaction, but I brought this up before several chemists and they seemed to think that titanium might very well perform in this same manner.

TABLE 2. STRESS-CORROSION CRACKING INDEX K_I_{SCC}
OF Ti-8Al-1Mo-1V ALLOY (T-19) IN
VARIOUS ENVIRONMENTS

Environment	K_I_{SCC} , ksi	$\sqrt{\text{in.}}$
Salt water.....	23	
Ethylene glycol.....	22	
Methanol.....	24	
Ethyl alcohol.....	34	
1-propanol.....	30	
1-butanol.....	30	
1-decanol.....	38	
2-propanol.....	36	
tert-butyl alcohol.....	40	
n-propane.....	35	
n-heptane.....	35	
n-hexane.....	40	

Obviously, a metal such as iron, which is not as active, would not be expected to react. So I am proposing that this first reaction may be playing a part in crack initiation in titanium alloys only.

I will summarize the evidence for this using only the information obtained from our smooth test specimens. We have found that titanium alloys crack in methanol, ethyl alcohol, and ethylene glycol, and as one would expect, all of these do react according to the first reaction. A small amount of water or glycerine in the alcohol greatly retards the reaction. Methanol and normal hexane do not crack steels. (I have not mentioned steels, but I should say that we have been unable to start a crack with methanol on 4340 steel heat treated to about 220 ksi yield strength in at least a 24-hour test at intensity levels only slightly below K_I_{SCC} , and

far higher than the K_I_{SCC} in saltwater.) One would not expect, according to this reaction, that methanol would crack a steel because it is not an active enough metal if that reaction applies. Normal hexane, of course, does not crack titanium and we would not expect that, since hexane is not an alcohol. Opposed to this, we have also been unable to start a crack in this titanium alloy using plain water. One possibility for this would be that, in a reaction, the product is insoluble and perhaps can seal off the titanium before a crack can really get started. Mr. Herrigel has suggested that, in case of alcohol, this reaction product would be soluble, but in water it would not. This is an important point.

In addition, the long-chain primary alcohols may not start cracks. The evidence we have is that we probably can start cracks as we get longer chains, but there again, the longer the chains, the more they behave like straight-chain hydrocarbons.

Now in the precracked specimens, the arguments favor the finding that the tertiary alcohol gives a higher K_I_{SCC} value. In other words, it would not be as active, and it so happens in this reaction that if you are breaking hydrogen off the chain, then one would expect that a tertiary alcohol would be much less active than a primary alcohol. Here again, methanol and hexane do not seem to crack steel even if we have a precracked specimen.

Opposed to this is our observation that, occasionally, even a tertiary alcohol gives low values of K_I_{SCC} . You see, if you suppose that a tertiary alcohol will not react according to this reaction, then how will you explain that it went from 85 ksi $\sqrt{\text{in.}}$ to, say, only 40 ksi $\sqrt{\text{in.}}$, even though a tertiary alcohol is less active than a primary alcohol?

We found that water does not propagate a crack in the Ti-6Al-4V alloy but methanol did. One might expect there again that straight-chain

hydrocarbons do propagate cracks in the titanium. So I need a second reaction here to explain the effects of the straight-chain hydrocarbons and suggest some sort of petroleum cracking reaction.

The chemists tell me that this may be possible in the presence of a fresh titanium surface and that a straight-chain hydrocarbon might crack to yield solutions containing unsaturated hydrocarbons and hydrogen. But still you can not explain the whole works with the cracking reactions because we could not start a crack with hexane on titanium. I am just saying that perhaps in the initiation of cracks the first reaction may take place, but it does not explain everything. Perhaps as you go to longer chain alcohols, or to the straight-chain hydrocarbons some sort of cracking reaction may have to take place. Both of these then are releasing hydrogen. I believe that the hydrogen is probably the bad actor in these reactions. We have seen that we can actually crack specimens in hydrogen. Other investigators have shown that when you anneal a piece of titanium in vacuum and lower its hydrogen content, that you also increase the $K_{I_{scc}}$ value.

**TITANIUM U-BENDS IN ORGANIC LIQUIDS,
EFFECT OF INHIBITORS**

by

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The work presented concerns the initiation (or lack of it) of stress-corrosion cracks in a variety of liquids, mainly organic, for five titanium alloys. (Ti-75A is here called an alloy of titanium). This type of study, rather than the more popular crack-growth study, was undertaken for several reasons, not the least of these being that it was less expensive and time-consuming. More technically persuasive considerations are:

- (1) The conditions chosen are representative of a combination of circumstances that could occur during fabrication of titanium parts.
- (2) With somewhat less likelihood, the same conditions might occur during the service life of a titanium structure.
- (3) Any complete explanation for stress-corrosion cracking of titanium must account for crack initiation as well as crack growth. We felt there was some value in determining whether the same agents that cause crack growth would cause crack initiation.

Titanium sheet in either 0.040 or 0.050 gage was used. Figure 1 illustrates the appearance of the samples used. One by 3-inch specimens were brake formed over a 0.56-inch-diameter mandrel to a Vee with an included angle of about 60 degrees. Due to spring-back, this Vee has a moderate tensile stress on the inside of the bend. For annealed Ti-6Al-4V, this stress is about 70,000 psi. To make the U-bend specimens for stress-corrosion testing, the legs of the Vee are pulled parallel and restrained with a stainless steel bolt through holes near the ends of the specimen. It is obvious that the metal is stressed to its yield strength in this specimen. If the restraint is relaxed, the specimen will be found to have taken a permanent set. For annealed Ti-6Al-4V, the set is about 12 degrees. Further, the specimen is seen to have yielded on the edges near the bottom of the U and assumed a slight saddle shape.

The U-bends were immersed in the liquid under test, and the time for cracking to occur recorded. Times recorded are for complete cracking-through of the specimens. This time for complete cracking is usually several minutes longer than the time at which the first indication of a crack can be seen.

The majority of the tests were conducted on mill-annealed Ti-8Al-1Mo-1V and annealed Ti-6Al-4V. However, in anhydrous methanol only, the following additional alloys and heat treatments were tested:

Ti-6Al-4V ST
Ti-6Al-4V STA 1000
Ti-5Al-2.5Sn annealed
Ti-4Al-3Mo-1V annealed
Ti-8Al-1Mo-1V, aged 1/2 hr at 1000 F
Ti-75A

Liquids tested were:

anhydrous methanol	n-butanol
methanol + water	n-butanol + water
methanol + nitrate	sealant, Dow
methanol + HCl	Corning 92024
anhydrous ethanol	paint stripper,
ethanol + water	wash-off, Parker-
ethylene glycol	Scott Co.
JP-4 fuel	butyl carbitol
JP-5 fuel	methyl ethyl
hexane	ketone
hydraulic fluid (Humble WSX-6885)	n-propanol
iso-propanol	trichloroethylene
iso-propanol + water	water, distilled
	water, Seattle
	tap
	water + 3.5% sodium chloride
	Freon NF

Test results are shown in Table 1. Crack initiation occurred only in those liquids listed in the table.

In addition to the cracking in methanol and ethanol, we have obtained cracking in some samples exposed to ethylene glycol. Specifically 3 of 9 Ti-8Al-1Mo-1V samples (taken in the transverse direction after heat aging for 1/2 hour at 1000 F in air) failed on exposure to ethylene glycol in about 0.4 hour.

This heat-aging treatment was developed in our laboratory as a means of sensitizing the Ti-8Al-1Mo-1V alloy and was adopted after inconsistent results were obtained with this material as received in the mill-annealed condition. A similar tendency was also noted for the Ti-6Al-4V alloy. That is, the as-received surfaces on these alloys seem to be more susceptible to crack initiation in that times to initiate and propagate cracking are shorter than for surfaces that have been acid cleaned and etched.

We get crack initiation in anhydrous ethanol, and I would like to stress that you have to be very careful to insure that anhydrous ethanol is anhydrous. We had some bottles of "anhydrous" ethanol that had been about half used with the screw cap kept securely in place. We did not get failures in this ethanol. However, with a fresh bottle of anhydrous ethanol, we did get the failures noted in Table 1.

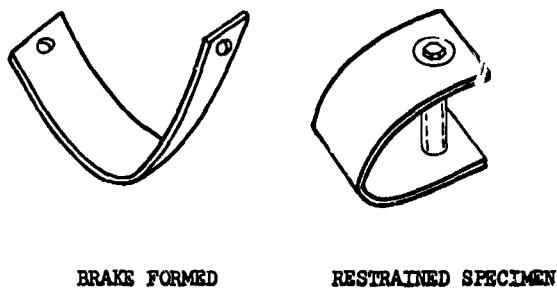


FIGURE 1. EXPOSURE OF RESTRAINED TITANIUM ALLOY SPECIMEN

We also noted that, for the Ti-8Al-1Mo-IV alloy, the susceptibility to cracking in methanol is greater in a transverse direction than for the longitudinal direction. Surprisingly, the reverse seems to be true for the Ti-6Al-4V alloy. The cracking time in the transverse direction, for the specimens that we have tested, is about twice as long in the transverse direction as for the longitudinal direction.

The stress-corrosion-crack initiation in methanol and ethanol can be suppressed by the addition of water. I do not know about the ethylene glycol, although I would suspect that this is also true. The ethylene glycol that we were using was ACS reagent grade (Baker's Analyzed) ethylene glycol.

In general, we have found that the addition of 2 percent of water to the methanol would inhibit the crack formation, and we also have evidence that the crack initiation and growth was slowed down quite considerably with something less than 1 percent of water. Thus, no failures were obtained in methanol containing 9,000 ppm of water and 5,000 ppm of HCl. Also, no failures were obtained where we had half that amount of water and half that amount of HCl.

We also found that stress-corrosion-crack initiation in the methanol can be suppressed by the addition of 10 ppm KNO₃ to the methanol. When we added as little as 10 ppm we had no failures in methanol even with the most susceptible alloy. We did not test the addition of nitrate to ethanol.

We have also tested the addition of sodium sulfate to the alcohol. Sodium sulfate is not very soluble in alcohol, and we are not sure as to exactly how much was present. If all that we added had dissolved, about 250 ppm sulfate would have been present at the higher

level and about 190 ppm of sulfate at the lower level. The sodium sulfate at the higher level did prevent cracking on some specimens. We had only about five specimens on test so our results here were not definitive. However, the sulfate appears to be effective in at least slowing the crack initiation and propagation.

All of the cracks appear to be brittle, except at the ends. Of course, as a crack runs out to the end of a specimen, a shear lip is observed. However, near the initiation point the lips appear to be brittle and from the initial work that has been done, they also appear to be transgranular.

The Ti-6Al-4V and Ti-8Al-1Mo-IV alloys were the only alloys that were tested at lower stress levels. Here, cracks did not initiate at the lower stress levels of 70 ksi.

Summarized, our tests show:

- (1) Crack initiation in (relatively) anhydrous methanol, in anhydrous ethanol, and in methanol with added water and hydrogen chloride. Cracks initiated in some specimens exposed to ethylene glycol. No crack initiation occurred in the other liquids tested.
- (2) All alloys and heat-treated conditions tested were susceptible to cracking in methanol. The order of decreasing susceptibility, as measured by increasing time to fracture, was:

Ti-8Al-1Mo-IV	mill annealed
Ti-5Al-2.5Sn	annealed
Ti-6Al-4V	annealed
Ti-6Al-4V	solution treated
Ti-4Al-3Mo-IV	annealed
Ti-6Al-4V	solution treated and aged
Ti-75A	
- (3) Susceptibility to cracking in methanol is greater in the transverse direction than in the longitudinal direction.
- (4) Susceptibility to cracking in methanol is increased by short-time aging at elevated temperature.
- (5) Stress-corrosion-crack initiation in methanol and ethanol can be suppressed by addition of 2 percent water:

TABLE 1

Liquid	Expected Time to Failure ^(a) , hours							
	Ti-8-1-1 Mill Annealed 140 YS	Ti-8-1-1 Mill Annealed Heat Age	Ti-5-2-5 Annealed 125 YS	Ti-6-4 Annealed 130 YS	Ti-6-4 St 145 YS	Ti-4-3-1 Annealed 120 YS	Ti-6-4 STA 145 YS	Ti-75A 70 YS
Methanol, anhydrous	0.8	0.4	1.6	4.9	9.4	10	15.8	60
		0.36 ^(f)			4.0 ^(c)			
		0.16 ^(g)						
Ethanol, anhydrous	5 ^(d)			29.4 ^(b)				
Methanol with 5200 ppm H ₂ O plus 2500 ppm HCl		24-45 ^(c)						
Ethyylene glycol			0.4 ^{(f)(h)}					

(a) Metal surfaces etch cleaned in HNO₃-HF except as noted.

(b) For one specimen, another specimen did not fail.

(c) As-received surface.

(d) For one specimen, somewhat greater than 5 for another.

(e) Failure times for two specimens. In methanol with 9700 ppm H₂O, 5000 ppm HCl, two other specimens did not fail.

(f) Transverse specimens, acid cleaned and heat aged.

(g) Transverse specimens, as received surface, heat aged.

(h) Three of nine specimens cracked.

(6) Stress-corrosion-crack initiation in methanol can be suppressed by addition of 10 ppm of potassium nitrate. Addition of nitrate to ethanol was not tested.

(7) The cracks appear to be brittle and transgranular.

(8) For Ti-6Al-4V and Ti-8Al-1Mo-1V, cracks do not initiate at a lower stress level of about 70,000 psi. The other alloys were not tested at stress levels below the yield.

Some miscellaneous observations should be mentioned. The time to fracture seems to follow a Poisson distribution. Some evidence exists, however, for two populations; one which breaks and one which does not. The crack usually starts at a spot in from the edge of the specimen, in the area of maximum stress. However, cracks started at the edge of some of the speci-

mens which had been aged in air. The crack, once initiated, takes several minutes to grow to complete failure. An initiated crack is difficult to stop. In one case, however, a crack initiated in methanol was stopped by immersion in isopropanol. This same crack grew rapidly to failure when the specimen was subsequently immersed in 3.5 percent salt solution.

I am sorry to say that I can offer no convincing mechanism to explain these observations. It is tempting to speculate on the fact that titanium is thermodynamically a very active metal, almost as active as magnesium, in acid solutions. Magnesium's reactivity with methanol is, of course, well known. It is of further interest that the tendency of the alcohols to initiate stress-corrosion cracks in titanium is in the same order as the reactivity rates of the alcohols in organic reactions. The lack of stress-corrosion-crack initiation in water, which might be regarded as the most reactive alcohol of all, may be related to the insolubility

of titanium hydroxide. Metal alcoholates, of course, are quite soluble in the alcohol.

In this connection, I recently noted one set of reactions in the literature that is of some interest. You might write this as titanium tetrachloride reacting with alcohol to form titanium alcoholate plus hydrogen chloride. The titanium alcoholate reacts with water to form a titanium hydroxide or a hydrated titanium hydroxide plus alcohol again. This is a reaction used commercially for flame proofing of fabrics. Of course, we know that there is some chloride remaining in all titanium alloys. This amount may vary from a few tenths to less than a tenth of a percent of chloride.* I suspect this chloride may exist as a titanium chloride and that it is randomly distributed. The fact that we did our tests with several different sheets of material and sheets of material from different companies may explain the considerable variability we found in the tendency for crack initiation to occur.

In any case, the test results reported here, when compared to the results of crack-propagation studies, indicate that in all probability more than one important mechanism is operative. A completely satisfying explanation of the phenomena has yet to be advanced.

* In later discussion, a TMCA spokesman indicated that the chloride content of titanium mill products was normally specified at 30 ppm, this amount being below the normal limits of detection.

THE INFLUENCE OF FLUOROCARBON SOLVENTS ON TITANIUM ALLOYS

by

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INTRODUCTION

The DuPont "Freon" Products Division became involved in titanium alloy studies because fabricators needed to know if fluorochlorinated solvents would cause cracking similar to trichloroethylene. Since fluorochlorocarbon solvents are very pure and thermodynamically more stable than the chlorinated solvents, there should be less chance for stress cracking from these compounds. To assist these titanium users, the effects of fluorochlorinated solvents on titanium alloys were studied under simulated use conditions. Trichloroethylene, methyl chloroform, and aqueous NaCl solutions were used as controls.

Specifications of two of the fluorochlorocarbon solvents considered in this presentation are presented in Table 1. Trifluorotrichloroethane is the prime fluorochlorocarbon solvent. It is used:

- (1) Alone for liquid and vapor cleaning as well as for pressure testing
- (2) In binary azeotropic combinations with acetone or methylene chloride for liquid and vapor cleaning
- (3) In water-in-solvent emulsion systems to remove water-soluble soils from surfaces.

The second solvent, trichlorofluoromethane, is used primarily for flushing and pressure testing.

For purposes of convenience, this presentation is divided into two parts which deal separately with the following subjects:

Part I: Highly stressed alloys

Part II: Highly stressed, precracked alloy
Fracture mechanics in materials evaluation

PART I THE INFLUENCE OF SOLVENTS ON HIGHLY-STRESSED TITANIUM ALLOYS

The following simulated alloy-exposure conditions were investigated:

- (1) Cleaning and pressure testing.
- (2) Exposure to liquid followed by drying and heating to 700 F or 1450 F. This simulates the situation in which a part is cleaned and then heated to

an elevated temperature.

- (3) Exposure to an atmosphere of solvent vapor at elevated temperature. This simulates the unintentional solvent entrapment in assemblies to be heated.
- (1) Simulated-Cleaning and Pressure Testing Conditions

The effect of refluxing solvents was determined by placing one stressed specimen in the vapor and one in the liquid of each refluxing solvent. After 24 hr, they were removed and examined. In addition, nonrefluxing fluids were also tested with the stressed specimen placed only in the liquid. These fluids were methyl alcohol tested at about 75 F, several concentrations of aqueous salt solutions tested at 118 F (the boiling point of trifluorotrichloroethane) and a water/detergent/fluorochlorinated solvent tested at 100 F. Each test system contained only one alloy. The results are summarized in Table 2.

Methyl alcohol was the only solvent that caused stress-corrosion cracking near room temperature. All four titanium alloys were compatible with the fluorochlorinated solvents. No cracking was encountered at room temperature with fresh inhibited methyl chloroform, trichloroethylene, or the several aqueous sodium chloride solutions.

- (2) Effect of Heating Solvent-Cleaned Alloys to 700 and 1450 F after the Solvents have Evaporated from the Surface.

Solvent-cleaned titanium alloys might be exposed to as high as 700 F in service and to 1450 F in annealing operations. Normally, the solvent will evaporate from the metal surfaces before exposure to these temperatures. Stressed specimens exposed to trifluorotrichloroethane, methyl chloroform, and aqueous solutions of sodium chloride showed the following results after drying and exposure to 700 F for 100 hr or 1450 F for 8 hr (Table 2):

- (a) No stress corrosion cracking was caused by any of the solvents or by the lowest concentration of salt residue on the alloys tested (less than 9 micrograms Cl⁻/sq in.).

TABLE 1. SPECIFICATIONS FOR FLUOROCHLORINATED SOLVENTS

White-room solvent grade of trifluorotrichloroethane (CCl₂FCClF₂)
 ("Freon" Precision Cleaning Agent^(a))

Purity: 99.9 wt percent minimum
 0.1 wt percent maximum of other fluorocarbons
 Residue content: not more than 1 ppm by weight (soluble + insoluble)
 Acid No. (mg KOH/g of sample): 0.003 maximum
 Cl : 0.1 ppm by weight maximum
 Moisture: 10 ppm by weight maximum

Solvent grade of trifluorotrichloroethane (CCl₂FCClF₂)
 ("Freon" TF Solvent)

Purity: 99.8 wt percent minimum
 0.2 wt percent maximum of other fluorocarbons
 Residue content: not more than 2 ppm by weight (soluble + insoluble)
 Acid No. (mg KOH/g of sample): 0.003 maximum
 Cl : 0.1 ppm by weight maximum
 Moisture: 10 ppm by weight maximum

Solvent grade of trichlorofluoromethane (CCl₃F)
 ("Freon" MF Solvent)

Typical analysis: 99.8 wt percent
 Typical residue content: 10 ppm by weight
 Cl : none when tested with an alcoholic solution of silver nitrate
 Moisture: 10 ppm by weight maximum

(a) "Freon" and combinations of "Freon" with numerals are DuPont's registered trademarks for fluorinated hydrocarbons.

TABLE 2. THE EFFECT OF ORGANIC SOLVENTS AND SODIUM CHLORIDE ON STRESSED U-BENDS OF TITANIUM ALLOYS

Fluid Applied	Exposure Environment and Results (a)					
	Exposed to Liquid Followed by Drying and Heating to 700 F		Exposed to Liquid Followed by Drying and Heating to 1450 F		Exposed to 1 Atm Vapors at 700 F for 100 Hr	
	24 Hr	No	No	No	No	No
Trifluorotrichloroethane (b)	Cracking	Cracking	Cracking	Cracking	Cracking	Cracking
Trichloro-fluoromethane (c)	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
Trifluorotrichloroethane / methylene chloride azeotrope (d)	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
Trifluorotrichloroethane / acetone azeotrope (e)	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
Inhibited vapor-degreasing-grade trichloroethylene	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
Inhibited white-room-grade methyl chloroform	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
+1 ppm aqueous Cl ⁻	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
+10 ppm aqueous Cl ⁻	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
+100 ppm aqueous Cl ⁻	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4	1, 2, 3, 4
Methyl alcohol, reagent grade	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3

(a) Alloys and heat treatments
(1) Ti-5Al-2.5Sn, mill annealed(2) Ti-8Al-1Mo-1V, mill annealed
(3) Ti-6Al-4V, solution treated and aged
(4) Ti-13V-11C₁-3Al, solution treated and aged

(b) "Freon" Precision Cleaning Agent, the white-room grade of "Freon" TF solvent.

(c) "Freon" MF solvent.

(d) "Freon" TMC solvent.

(e) "Freon" TA solvent.

(f) "Freon" TWD 602 solvent - objects cleaned with this solvent are always followed up with a rinse in "Freon" TF solvent

() "Freon" and combinations of "Freon" with numerals are DuPont's registered trademarks for fluorinated hydrocarbons.

- (b) The salt residue from 400 ppm Cl⁻ (20 µg Cl⁻/sq in.) microcracked Ti-8Al-1Mo-1V, Ti-5Al-2.5Sn, and Ti-13V-11Cr-3Al at 700 F.
- (c) The salt residue from 4000 ppm Cl⁻ (110 µg Cl⁻/sq in.) microcracked all four alloys at 700 F. Only Ti-13V-11Cr-3Al was microcracked at 1450 F. Stresses are relieved by annealing at 1450 F.

Methyl chloroform was tested as an example of an inhibited chlorinated solvent. No cracking was found on U-bends that were exposed to the solvent, dried, and heated. It is suggested that any conclusions about the stability of the inhibited solvents (trichloroethylene and methyl chloroform) be limited to fresh solvent applications only, since inhibitors become exhausted during use.

(3) Effect of Organic-Solvent Vapors at 1 Atmosphere of Pressure on Titanium Alloys at 700 F for 100 Hours and 1450 F for 8 Hours

In some situations, solvents may be left unintentionally in alloy assemblies and later be exposed to elevated temperatures. These situations were simulated as follows:

- (a) At 700 F, sufficient solvent was added to a vented Pyrex flask to give approximately 1 atmosphere of pressure at the test temperature.
- (b) At 1450 F, sufficient solvent was added to give approximately 1 atmosphere of pressure of solvent vapors at 1450 F in a vented steel cap and nipple assembly which had been previously purged with helium.

All but the trifluorotrichloroethane/water/detergent solvent were tested at 700 F. This solvent was not tested since the items cleaned with this solvent are always rinsed off with trifluorotrichloroethane. The results were (Table 2):

- (a) The fluorochlorinated solvents did not cause stress cracking.
- (b) Trichloroethylene caused microcracking of Ti-8Al-1Mo-1V and severe cracking of Ti-5Al-2.5Sn
- (c) Methyl chloroform caused severe cracking of all four alloys.

Only the most stable solvent, trifluorotrichloroethane, was tested at 1450 F. This solvent caused some cracking of all four alloys. It is assumed that the other solvents, which are less stable, would also cause cracking at 1450 F.

One result of this work is that the trifluorotrichloroethane cleaning process was adopted by a large titanium fabricator. To be certain no cracking will occur because of liquid entrapment, a hold time for drying has been introduced between the cleaning and the heating step.

Summary

The four titanium alloys are compatible with the fluorochlorocarbon solvents under normal cleaning conditions and unintentional solvent vapor exposure up to 700 F. The test alloys cleaned with these solvents also may be exposed to temperatures of 1450 F, provided that reasonable care is taken to remove solvent entrapped in items such as spheres, cylinders, and tubes. Solvent volatility simplifies vapor purging.

The alloy are compatible with fresh inhibited methyl chloroform and trichloroethylene under normal cleaning conditions, but are subject to stress-corrosion cracking in the presence of solvent vapors at 700 F.

Salt residue can cause stress-corrosion cracking at both 700 F and 1450 F.

The Ti-6Al-4V is the least susceptible to stress-corrosion cracking by the agents tested.

PART II THE INFLUENCE OF ORGANIC SOLVENTS ON TITANIUM ALLOY (USE OF FRACTURE MECHANICS FOR MATERIAL EVALUATION)

It was shown in Part I that methyl alcohol was the only solvent which caused stress-corrosion cracking of U-bend specimens exposed to the liquid at room temperature. These specimens were free of detectable cracks or defects. When cracks or flaws are present, fracture mechanics can be applied to study the effect of environment. In air a sample containing a crack will fracture at a calculatable stress-intensity level. The stress intensity, K, is expressed as ksi $\sqrt{\text{in.}}$ (kilopounds per square inch $\sqrt{\text{inch}}$) (see Figure 1) and relates the stress level to the crack or flaw size in the material. It has previously been found that cracks present in some titanium alloys will propagate in salt-water at a stress-intensity level which initially is lower than found in air. The crack propagates slowly until the value of K for failure in air is attained at which time the remaining metal will fracture rapidly. The value of K, for initiation of crack propagation, can be compared with that for fracture in air to provide a measure of the effect of the environment. This approach was used in this study to determine the effect of solvents on precracked titanium alloys.

Mechanical fatigue cracking or notching could initiate this type of environmentally induced cracking in a susceptible alloy. The greatest environmental effect occurs when the mode of fracture is plane strain. As the sheet thickness increases, the percent of plane strain

fracture also increases. It is believed that the samples used in this study approach plane strain fracture. The materials used are given in Table 3.

Conclusions (see Table 4)

- (1) Ti-6Al-4V and Ti-13V-11Cr-3Al are not sensitive to environmental cracking in trifluorotrichloroethane at room temperature or at the solvent boiling point. The stress intensities for initiation of crack propagation were reduced 10 percent or less from those found for fracture in air.
- (2) Ti-5Al-2.5Sn and Ti-8Al-1Mo-1V are susceptible to crack propagation in certain environments. The stress intensity for crack initiation was reduced when these alloys were exposed to uninhibited chlorinated and fluorochlorinated solvents, aqueous salt solutions, and methyl alcohol.
- (3) Chemical additives can minimize the solvent effect on the Ti-5Al-2.5Sn and Ti-8Al-1Mo-1V. The stress-intensity for cracking was lowered by uninhibited methyl chloroform but not by inhibited methyl chloroform.

Discussion

A compilation of the stress-intensity data is provided in Table 4. Coordinates (K , time) are indicated for cracking and for the maximum stress intensity which did not cause cracking.

The environmental effects found using fracture mechanics apply only when sharp notches approaching fatigue cracks are present in parts to be cleaned or pressure tested. It is felt that because of poor welds or other fabrication faults, some structures with cracks will be exposed to solvents. Cracking will occur if K is above the threshold K for crack propagation in the solvent. Mathematical techniques are available for determining the stress-intensity on the part. Fortunately, it is anticipated that few structures being cleaned or pressure tested will have the necessary conditions for environmentally-caused crack propagation. If environmental cracking is found to occur, chemical additives are available to inhibit it. Variables other than environment and composition of the alloy also may affect the stress-intensity required for crack propagation. They include:

- (1) Heat treatment
- (2) Sample orientation
- (3) Sample thickness
- (4) Stress magnitude and orientation

(5) Presence and size of sharp cracks.

It is not clear whether U-bend or pre-cracked samples present the more realistic evaluation of a solvent to be used for cleaning and pressure testing titanium alloy parts. Methyl alcohol is such a case. Methyl alcohol at ambient temperature causes cracking of U-bends as mentioned earlier and also has cracked a Ti-6Al-4V tank. However, methyl alcohol does not lower the stress intensity for crack propagation as much as do some solvents which have no effect on U-bend specimens. Until more is known on the merits of these test methods, it is desirable to use only solvents which have the minimum tendency to crack both U-bend and precracked specimens of the alloy being used.

Experimental

The test apparatus and sample geometry (a) are similar to those developed by B. F. Brown to study the effect of salt water on the propagation of cracks in metals. The specimen is a rectangular bar provided with a V-notch and fatigue extension. Side grooves have been provided to direct the crack as it propagates. The environment was contained in a polyethylene bottle which was sealed around the bar by heating and reinforcing with epoxy cement. Reflux conditions were simulated by heating the liquid with an immersion heater inserted through the top of the bottle. Figure 2 shows the type of cracking that occurs with certain alloys affected by environment. The fatigue crack was introduced by flexing the sample in a lathe. The region C-D shows the extent of environmentally induced cracking prior to final rapid fracture. During testing, one end of the specimen is clamped to the frame of the rack and the other end is clamped to the lever arm from which is suspended a bucket containing weights. The testing is conducted by adding the load in step increments. The time to cause failure at the maximum load is recorded as well as the time where failure did not occur at one load increment under the maximum load. Properties of the alloys are listed in Table 3.

(a) B. F. Brown, Materials Research and Standards, 6, 129 (1966)

TABLE 3. SUMMARY OF TITANIUM ALLOY PROPERTIES

Alloy -----	Ti-5Al-2.5Sn	Ti-8Al-1Mo-1V	Ti-8Al-1Mo-1V	Ti-13V-11Cr-3Al	Ti-6Al-4V	Ti-6Al-4V
Treatment	Mill ^(a) annealed	Mill ^(b) annealed	Duplex ^(c) heat treatment	Solution ^(d) treated and aged	Solution ^(e) treated and aged	Mill ^(f) annealed
Thickness of As-Received Sheet, inch	0.125	0.125	0.125	0.125	0.125	0.950
Heat Number ^(g)	D-7905	D-8733	From D-8733	D-8896	D-8086	D-6675
Composition, percent						
C	0.025	0.023		0.021	0.026	0.023
Fe	0.27	0.08		0.20	0.10	0.06
N	0.013	0.011		0.013	0.016	0.015
Al	5.1	7.8		3.0	5.8	5.8
V	-	1.9		13.6	4.0	4.1
Cr	-	-		10.8	-	-
Mo	-	1.1		-	-	-
H	0.008	0.008		0.007	0.007	0.005
Sn	2.6	-		-	-	-
Mn	0.004	-		-	-	-
O	0.19	0.10		0.14	0.13	0.11
Yield Strength, ksi						
Longitudinal	124.5	154.1		192.5	153.2	120.0
Transverse	127.9	148.9		192.2	160.7	134.9
UTS, ksi						
Longitudinal	129.5	159.2		213.8	167.4	130.1
Transverse	131.1	157.5		211.1	173.3	142.2
Elongation, percent						
Longitudinal	16.5	14.0		7.0	9.0	15.0
Transverse	17.0	14.0		6.5	13.0	16.0

- (a) Ti-5Al-2.5Sn - An α alloy (hexagonal, close-packed lattice). Mill annealed at 1,325 F for 4 hours, then furnace cooled.
- (b) Ti-8Al-1Mo-1V - A near α alloy. Mill annealed at 1,450 F for 8 hours, then furnace cooled.
- (c) Ti-8Al-1Mo-1V - Duplex heat treatment. The as-received mill annealed sheet (b) was heated for 1 hour at 1,750 F and air cooled, followed by a 15-minute stress relief at 1,100 F and again air cooled.
- (d) Ti-13V-11Cr-3Al - β alloy (body-centered cubic lattice). Solution treated and aged; annealed at 1,450 F for 15 minutes and air cooled, plus aged, at 900 F for 24 hours and air cooled.
- (e) Ti-6Al-4V - α/β alloy. Solution treated and aged; annealed at 1,670 F, water quench; then aged for 4 hours at 1,000 F followed by air cooling.
- (f) Ti-6Al-4V - α/β alloy. Mill annealed. The probable heat treatment involved a mill anneal around 1,450 F for 1 to 8 hours followed by a furnace cool to 1,050 F and finally an air cool to room temperature.
- (g) Alloys obtained from Titanium Metals Corporation of America.

TABLE 4. INFLUENCE OF ENVIRONMENTS ON TITANIUM ALLOY STRESS INTENSITIES REQUIRED FOR CRACKING

Note: Units are stress intensity factors, K, ksi $\sqrt{\text{in.}}$ and time in minutes. Except where noted, sample loaded in liquid.

Environment	Ti-6Al-4V(a)				Ti-13V-11Cr-3Al(a)				Ti-8Al-1Mo-1V(a)				Ti-5Al-2.5Sn(a)			
	Solution Treated and Aged		Mill Annealed		Solution Treated and Aged		Mill Annealed		Failure Values		Nonfailure Values		Failure Values		Nonfailure Values	
	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min	Failure Values K, min	Nonfailure Values K, min
Air - room temperature	51, 0.3 47, 0.5 54, 0.3	48, 1.5 44, 1.0 49, 1.0	66, 1.3 60, 1.3	--	37, 0.3 36, 0.1 31, 1	-- 29, 15 --	42, 1.5 37, 1 31, 5	-- 28, 15 30, 15	82, 2 91, 0.3	-- 88, 10	78, 15 69, 6.5	-- 73, 10	77, 0.8 69, 6.5 65, 10	-- 73, 15 65, 10		
Distilled water - room temperature	--	--	--	--	--	--	32, 8.5	28, 15	--	--	--	--	73, 1	69, 10	26	
0.05 wt % NaCl in distilled water - r.t.	--	--	--	--	--	--	--	--	--	--	--	--	49, 2.3	46, 10	--	
0.1 wt % NaCl in distilled water - r.t.	--	--	--	--	--	--	30, 1.5	25, 10	--	--	--	--	44, 2.8	41, 10	--	
3.5 wt % NaCl in distilled water - r.t.	49, 0.3	46, 1.5	--	--	--	--	27, 2.3	23, 15	--	--	--	--	31, 1.5	28, 15	--	
Trifluorotrichloro-ethane, (c) r.t.	54, 0.4	49, 2.5	56, 5 53, 10.8	51, 10	--	--	23, 15.3 23, 10.8	--	52, 2.8 44, 10	--	51, 15 41, 15	--	31, 8.5	28, 15	--	
Trifluorotrichloro-ethane, (c) boiling pt.	52, 2 52, 0.5	48, 1.0 --	--	--	38, 1.5 34, 4 32, 0.5	32, 10 31, 15 --	--	--	--	--	--	34, 2.3 30, 3	--	--		
Trifluorotrichloro-ethane, (c) boiling pt. Sample loaded in air	--	--	--	--	--	--	--	--	--	--	--	36, 2.3	-- 34, 25 34, 20	--		

Trichlorofluoromethane(d) room temperature	--	25, 3.2	--	--	26, 1.7	22, 15	--	--	24, 2.8	22, 15
Methyl chloroform (inhibited) r.t. (white-room grade)	--	--	--	--	37, 3.2 32, 21	33, 15 29, 15	--	--	74, 0.5 71, 1	67, 18 68, 15
Methyl chloroform (uninhibited) r.t.	--	--	--	--	--	--	--	--	28, 2.3	25, 15
Trichloroethylene (inhibited) r.t.	--	--	--	--	28, 19.7	23, 15	--	--	--	--
Methyl alcohol (Reagent grade) r.t.	--	51, 15	--	--	33, 2	27, 15	--	--	43, 0.5 37, 1.0	39, 10 36, 60
Octafluorocyclobutane(e) boiling point	--	--	--	--	--	--	--	--	49, 5.5	48, 5

(a) 1/8-in. plate. Specimen cross section 1 x 1/8 in. Long dimension parallel to longitudinal rolling direction. Crack propagation occurred in the transverse rolling direction.

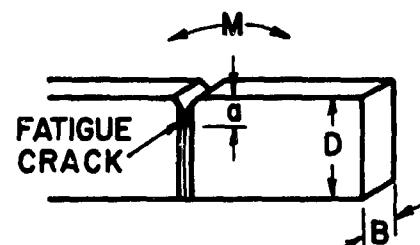
(b) 1-in. plate; specimen section 1 x 1/2-in. Crack propagation occurred in the through-the-plate direction. Orientation of long dimension of sample with respect to rolling direction is unknown.

(c) "Freon" TF solvent (CCl_2FCClF_2).

(d) "Freon" MF solvent (CCl_3F).

(e) "Freon-C318" fluorocarbon (cyclic C_4F_8).

"Freon" and combinations of "Freon" with numerals are Du Pont's registered trademarks for fluorinated hydrocarbons.



$$K = \frac{4.12 M \sqrt{\frac{1}{\alpha^3} - \alpha^3}}{B D^{3/2}}$$

$$\alpha = 1 - \frac{a}{D}$$

K = kilopounds per square inch

M = kilopound-inch

D = 1 inch

B = 1/8 or 1/2 inch

(See note below)

FIGURE 1. EQUATION USED TO CALCULATE STRESS INTENSITY FACTOR, K FROM B.F. BROWN ET AL

NOTE:

On some samples, the fatigue crack had a thumbnail appearance rather than being of uniform depth. The dimension a was then taken at the maximum depth.

The thickness, B, was normally 1/8 in., which was the plate thickness, or 1/8 in. less the side grooves. The total thickness was used on those samples where the crack did not follow the side grooves.

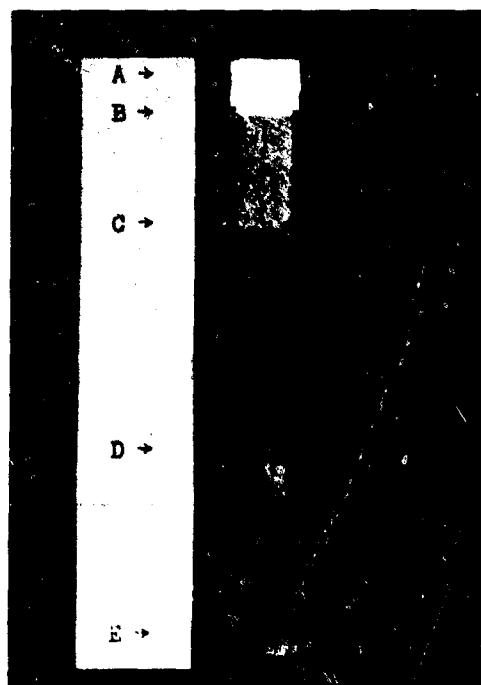


FIGURE 2. Ti-5Al-2.5Sn CROSS-SECTIONAL VIEW OF FRACTURE OF CANTILEVER SPECIMEN

- A-B machined V-notch
- B-C fatigue crack
- C-D stress-corrosion cracking band
- D-E final rapid fracture

**DISCUSSION OF FAILURE ANALYSIS AND RELATED PROBLEMS
ON TITANIUM PRESSURE VESSELS**

by

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I would like to preface my remarks by stating that our program at General Electric was simply involved with a failure and analysis problem on a titanium pressure vessel. No research or development effort was authorized or engaged in. Our effort was directed at getting an immediate fix and obtaining a maximum reliability assurance level as quickly as possible.

Table 1 shows the two pressure-vessel designs involved - the first was the design we had our failure problems with; the second gave us additional problems which we found and I think solved very, very quickly, so that we had no failures whatsoever on our second design. The first design was for a Ti-7Al-4Mo alloy; the second was for the Ti-6Al-4V alloy.

Design 1 was forge welded using the Uni-weld process; Design 2 contained a fusion weld that was made in an argon chamber. We added additional requirements to our second design in that we limited the ultimate strength to 160,000 to 180,000 psi, the yield strength to 150,000 psi, and elongation to 10 percent minimum. We added three specimens from each hemisphere; one of them was a smooth tensile specimen; the second had a notch to meet the requirements of 125 percent of the ultimate strength, and the third was a notch-time-rupture specimen. We also added an engineering equation that the tank had to meet; that is, wall thickness (of each hemisphere) times the ultimate strength had to exceed a value of 38,245.

As per specification, three units were selected for acceptance and qualification testing. The results were in conformance with the requirements of the specification. Based on these results and on the results of acceptance tests on individual units, the tanks were accepted by General Electric for prime use in the vehicle in July of 1963.

Upon completion of the assembly of the stabilization system, and to assure system reliability, the mechanism was proof pressure tested with Freon 114. Five stabilization systems had been tested without incident; the sixth system failed, as tank S/N 40 burst. This tank, which had been acceptance tested by Vendor 1 at 5400 psi with water at room temperature, burst 1 minute after the system had been brought to the proof pressure of 5250 psi at General Electric, this proof pressure being only 73 percent of the tank's rated burst pressure. The failure of tank S/N 40 precipitated an intensive failure investigation.

The failure initiation site, shown in Figure 1, was located by tracing the "chevron" patterns (illustrated in Figure 2) to the point of convergency, this point being the origin of failure. As indicated in Figure 1, the failure originated on the ID of the tank, propagating through the tank wall thickness and then throughout the tank. A series of discontinuities were located at the failure initiation site which were 0.042-inch deep and 0.100-inch long. These defects triggered the reaction which precipitated the tank failure. Microexamination of the discontinuities failed to detect any discrepancies in the underlying metal structure or to cast any light on the nature of these apparent imperfections. A hypothesis was set forth that the discontinuities were originally microcracks which "grew" as a result of the mechanism that produced the failure.

The reexamination of the tank's X-ray films, taken by Vendor 1 in fulfillment of the specification requirement, did not reveal any discontinuities or defects; however, because the sensitivity of the X-rays (i.e., the film grain was only 2 percent), flaws smaller than 0.010 inch in depth are not detectable. As determined by metallographic techniques, the discontinuities believed to be responsible for the failure are much less than 0.010 inch.

Test programs were initiated to determine the exact mechanism of failure. I will not go into the test programs or data, or the nightmare that followed. The report is available.* At the same time, to determine if the failure obtained was random, another tank was proof tested. This tank also failed.

Based on the theory of fracture of high-strength materials (UTS of 200,000 psi), previous experience at GE Evendale with Ti-4Al-4Mo titanium alloy, and preliminary results of the mechanical testing to this time, a decision was made to anneal five tanks. The cycle was vacuum anneal at 1450 F-1 hr, cool in vacuum at a max rate of 5 F/min to 1050 F, and air cool to room temperature.

To evaluate the effect of this annealing cycle, Tank 7 was proof pressure tested at 4250 psi with Freon 114. After being at pressure for 1 hour the tank burst. The fracture appearance was similar to that of the other failed tanks,

* Limited availability; please contact author.



40,000X

1μ

FIGURE 1. TRANSVERSE SECTION OF Ti ALLOY SPHERE NEAR FRACTURE INITIATION SITE.

Inner Spherical Surface is on Right. Note Network of Cracks.



FIGURE 2. CHEVRONS WITH SHEAR LIP (TYPICAL)

with the exception that there appeared to be a large number of initiation sites rather than a single distinct location.

This phenomenon was attributed to sites initiating as a result of the stress wave which precedes the propagating crack. The prior existence of a series of discontinuities in the metal structure was necessary to produce the fracture appearance observed.

As with the other failed tanks, the results of the preliminary failure analysis were negative; hence, the aforementioned program was expanded to include this material. In addition, since this was an annealed tank, the expanded program included mechanical tests to ascertain the effectiveness of the annealing procedure.

Electron microscopy on the failure initiation site reveal that:

- (1) Many microcracks were present, probably formed by the manufacturing process due to the high local stress at or near the forge-weld location.
- (2) If the geometry of the tip of the crack is proper, the crack may behave as a severe notch in a tensile specimen. Upon pressurizing the vessel, the stress concentration in the vicinity of the tip of the crack may become sufficiently great as to result in crack propagation and failure. This would be most plausible for a completely brittle material. Since the titanium alloy is ductile, it appears most likely that many microcracks combine, during pressurizing of the vessel, to form a critical size notch which then propagates as a failure crack. This type of failure would be expected in a region in which microcrack density is high (weld vicinity).

The sphere which survives the water pressure test may fail the Freon 114 test at a lower pressure for the following reason: The chlorinated Freons are potentially more chemically active than the saturated fluorocarbons. When an active substance is absorbed on the tip of a crack in a material under stress, then the material in this region may be weakened through chemical alteration. The stress concentration in the vicinity of the tip of the crack may then become sufficiently high that the crack is propagated. This is believed to be the reason why the vessels which survived the high-pressure water testing, failed with Freon 114.

During the routine proof pressure testing of a vehicle's stabilization system, comprising a Ti-7Al-4Mo cold gas storage tank, the tank burst; the failure occurred at a pressure of 5250 psi, which was 73 percent of the tank's rated burst pressure.

The investigation, initiated to determine the mode of failure, revealed that the tank alloy was notch-time-rupture (NTR) sensitive, i.e., a notched specimen ($K_t = 5.4$) of the alloy when stressed to 71 percent of the material's ultimate tensile strength would fail, not on loading, but with time.

Tests were run which demonstrated that a "notch" is required to initiate the reactions which ultimately result in failure. Electron fractographs of the failure initiation sites revealed that the notches which were precipitating the failure were microcracks; the formation of the microcracks was believed to have occurred during the forge welding operation. The location of the failure initiation sites at the forge weld is attributable to the following conditions:

- (1) The NTR sensitivity of the alloy
- (2) The presence of notches (micro-cracks)
- (3) The point of highest stress - 148,500 psi at a tank proof pressure of 5250 psi.

Evaluation of the influence of test conditions on notch-time-rupture strength demonstrated that Freon 114, the test pressurant that is utilized in place of the operating fluid Freon 14, adversely affects, while temperature improves, the NTR strength (the average stress at which failure will occur on constant notch specimens).

Since the NTR strength under the Vendor acceptance test procedure (water at 200 F) is 152,000 psi, and under the GE systems test procedure (Freon 114 at R.T.) is 117,000 psi, the probability of failure of the tanks under the former test procedure is decreased.

Since a Freon 114 atmosphere resulted in a reduction of the notch-time-rupture strength of the Ti-7Al-4Mo alloy, tests were run to determine if Freon 14, the operating fluid, exhibits the same deleterious effects. Limited test results, along with information derived from the literature, suggested that Freon 14 does not materially effect the notch-time-rupture strength of this titanium alloy.

A rough correlation exists between the NTR sensitive tanks and the alloy heat numbers from which the units were manufactured. Of the 44 tanks included in this first order, 26 were obtained from material which is suspected of being NTR sensitive. The data available on tanks manufactured from a particular heat of material indicate that the greater percentage do not exhibit NTR sensitivity and/or do not contain a critical crack. Hence, a pressurization screening test was defined and instituted to eliminate defective units.

The screening test (9 cycles at 5400 psi plus a 48-hour hold at 5400 psi with water at 75 F) is capable of "culling out" tanks which are NTR sensitive and/or contain a critical crack. The duration of this test cycle precluded the acceptance of tanks which were damaged (as evidenced by crack extension) during the test cycle. The tanks were pressurized during operation to a maximum wall stress of 99,000 psi versus a stress of 152,700 psi in the test cycle, thus providing a reasonable factor of safety in using tanks which pass this screening test.

Two tanks failed in the screening test. All others were accepted as prime units and performed reliably.

A second contract was let for Design 2 by Vendor 2, for Ti-6Al-4V vessels. No serious problems developed and the units were accepted for prime use. Eight tanks were involved in this first order. Additional orders were placed and no failure problems occurred. Our specifications and quality assurance provision had been designed to include a consideration of all variables in the material, manufacture and testing of pressure vessels, and to provide assurance of reliability. Certain variables are difficult to identify or clarify to the degree where a definitive evaluation of magnitude of variable is possible and cannot be included in our design or acceptance criteria. These may be a defect caused by a process too small to identify in inspection, or a material response not accounted for in our metallurgical knowledge.

Tank S/N 05 was burst (qualification test) at 7950 psi at 200 F. Based on the formula $S = \text{yield (min)} X 2T = 150,000 \times 0.464 = 7240 \text{ psi}$

Radius 9.6

at R.T. Using the design engineering correction for 200 F = 6360 psi, the tank failed 9.2 percent over the yield. Based on our new formula for acceptance, $S (\text{min}) = 0.238 \times 172,000 \text{ psi} = 40,936 \text{ psi}$; this value was well above the minimum of 38,245 psi for acceptance. Yet the tank failed at the weld through a defect (inclusion). Based on the data presented by design engineering, failure of the tank should occur at the point of highest hoop stress at or near the weld and parallel to the weld. In fact all three burst test tanks failed in the same manner, perpendicular to the weld. Defects in the welds propagated or opened up during the mechanism of failure, yet did not cause failure. None of these defects were picked up in any of the inspection tests, due to their size. The safeguard incorporated in the QAP (quality assurance provisions) notch tensile and notch-time-rupture tests indicate that unless there are defects large enough, the sensitivity to notch failure is low enough to resist propagation and initiation of failure. If the notches are large enough, they will be picked up in the required inspection. No attempt has been made to develop a "notch sensitivity level" number which could be used as a yardstick for quality. Data accumulated on our pressure vessels indicate a low notch sensitivity as compared to our previous tanks of Ti-7Al-4Mo. However--one discrepancy

appeared, between the first group of eight tanks and all others after #8. See Table 2.

The difference between the first group of tanks and the second group was in oxygen content of the alloy. We investigated notch size, depth, radius, finish, method of testing specimens, and even investigated the test technician to find an answer to the difference in notch time rupture. We found no answer.

In titanium alloys, a higher oxygen content produces a higher physical property in the material with heat treatment. The original properties were developed with an oxygen content of 0.10 percent or less. The presently higher physical properties developed in the later tanks are due to the higher oxygen content of 0.18 percent, which is allowable under the specification. In all probability, the structure of the material is also affected by the forging process (and the higher oxygen) so that to produce an ultimate tensile in the 160,000 to 170,000 psi range either the oxygen content must be restricted to below 0.10 percent if possible, or the aging (tempering) temperature must be raised. It was found necessary to raise the tempering temperature to bring the ultimate down to specification of 160,000 - 180,000 psi. We know that as a result of a higher tensile strength (i.e. 180,000 to 190,000 psi ultimate), a lower elongation and less ductility are achieved. The result will unavoidably be accompanied by a higher notch-time-rupture sensitivity which will be more adversely affected by the presence of defects or notches of a lower magnitude. Note however, that the ultimate strength value of material from tank 15 is the same as that from tank 02, yet the difference in NTR is present.

We believe that this is a significant point which should be thoroughly investigated. We believe that Freon 114, methanol, and other fluids are degrading very slight defects to a greater magnitude. We believe that the manufacturing processes are developing slight defects in the materials which are basically the initiation sites of failure which are triggered and which produce the failure mode.

If our purpose is to find and identify any and all contributors to the mechanism of failure, then our investigations must not be closed with the elimination of detrimental cleaning processes or operating fluids.

TABLE 1. PNEUMATIC STORAGE TANKS

Drawing:	General Electric:	19-in diam. (approx)	
		1/4-in wall (approx)	
		2 forged hemispheres.	
Material:	Design 1	- Ti-7Al-4Mo	
	Design 2	- Ti-6Al-4V	
Welding:	Design 1	- Forge weld, Uniweld (air).	
	Design 2	- Fusion, argon chamber.	
Tank Requirements:	UTS, psi	YTS, psi	EI, %
1	185,000 min	165,000 min	5 min
2	160 -180,000	150,000 min	10 min
2 additional	- each hemisphere		
Min. wall thickness X UTS = 38,245 psi (min)			
Smooth tensile specimen			
Notch specimen(125% of UTS) (3.7/4.1 K _t)			
Notch time rupture specimen			

Pressurant: Freon 14

TABLE 2. PROPERTIES OF TANKS

Tank	Hemisphere	UTS, psi	Strength, psi, Notch	Average Notched Stress and Time to Failure
02	1	172,000	289,000	280,000 psi @ 67 hours
	2	172,000	272,000	270,000 psi @ 64 hours
21	57	185,000	234,000	250,000 psi @ 46.5 hours
	40	181,000	251,000	240,000 psi @ 46.1 hours
15	27	174,000	247,000	240,000 psi @ 45.6 hours
	11	169,000	244,000	240,000 psi @ 44.7 hours

Difference in chemistry

Tank	Oxygen Content, percent
02	0.10
21, 15	0.18

**PRELIMINARY TEST DATA ON TITANIUM-METHANOL
STRESS CORROSION PROBLEMS**

by

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I would like to describe very briefly some tests we have conducted so far on the titanium stress-corrosion problem in methanol. These have been concerned primarily with Ti-6Al-4V sheet in the annealed condition, although we have conducted a few tests on the solution-treated-and-aged alloy, as well.

The specimens that we have utilized are of the double-bow configuration with weld constraint imposed at each end (as described in reference 1). With this type of sample, maximum stress is obtained in the outer fiber and is determined by the radius of curvature imposed by the end constraint as well as the thickness and elastic modulus of the material. Specimen stresses that we have investigated so far have been 50 to 100 ksi. In the experimental procedure which we used, the specimens were made up and exposed to methanol, with various additions, in glass beakers. The beakers were covered with plastic to prevent water pickup. In one series of tests, solutions containing additions of HCl to methanol to give HCl concentration of 0.10, 0.010, and 0.001 percent by volume were used. Tests were also conducted in sodium chloride solutions with chloride equivalents equal to those of the HCl tests. We have also conducted tests in reagent-grade methanol and in spectrographic-grade methanol for control purposes.

Results, based on about 50 tests, with annealed Ti-6Al-4V stressed at 50 and 100 ksi in reagent-grade and spectrographically pure methanol showed that no failures of the base material occurred after exposures of 90 days.

Failures were observed in annealed Ti-6Al-4V specimens exposed to the various chloride-containing methanol solutions and for all of the HCl concentrations investigated, i.e., from 5 to 20 hours for the 100-ksi specimens, and from 50 to 200 hours for the 50-ksi specimens. The specimens that were exposed to sodium chloride at 100 ksi appeared to fail in only slightly longer times than with the HCl additions at the same concentration.

I made approximately five to ten tests on solution-treated-and-aged Ti-6Al-4V material, and failures of these were observed in the reagent-grade methanol after approximately 15 hours exposure. However, with additions of HCl from 0.10 to 0.001 percent, failures occurred in 5 to 10 minutes.

On examination of all of these failed specimens, the only cracks that we could observe

were those which caused failure itself.

Now just a few comments on the Ti-0.2 Pd alloy. We found no effect with reagent-grade and spectrographically pure methanol. However, with small concentrations of chloride present in the methanol, this alloy suffered severely by blistering and general degradation and finally dissolution. It was obvious that the attack was much more pronounced in 0.10 percent chloride solution, somewhat less in 0.010 percent chloride, and still less in 0.001 percent chloride. However, the attack was still sufficient at the 0.001 percent concentration to cause complete degradation of this material in approximately 2 weeks.

(a) A few of these specimens did fail in the heat-affected zone of the welds that were used to restrain the ends.

REFERENCE

- Heimerl, G. J., and Braski, D. N., "A Stress Corrosion Test for Structural Sheet Materials", Materials Research and Standards, Vol 5 No. 1, (1965)

SUBCRITICAL CRACKING OF TITANIUM ALLOYS
AND HIGH-STRENGTH STEELS IN ORGANIC ENVIRONMENTS^(a)

by

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At Battelle Northwest Laboratories, we have been studying the problem of subcritical cracking or delayed failure for several years. Due to the nature of hydrogen in causing slow crack propagation in high-strength steels, our original efforts were on D2 tool steel to determine the mechanism by which this problem occurred, and to extend these studies to other materials as our technique was refined. It was found that the external atmosphere or environment in which tests were conducted determined to a great extent the rate at which crack propagation occurred in high-strength steels, zirconium alloys, and titanium alloys. Further studies on the effect of environmental factors led us to the study of the effect of various organic solvents on the crack-propagation rate of high-strength steels and titanium alloys.

The double cantilever beam specimen has been developed for use in our tests by Hoagland.⁽¹⁾ Figure 1 is a schematic of the double cantilever beam (DCB) specimen. The specimen is crack line loaded with sharp side grooves running down the length of the crack plane. The side grooves keep the crack running down the center of the specimen and serve as a means of providing a triaxial state of stress at the crack tip. A compliance relationship relating the load, extension, and crack length of the specimen was developed by Hoagland both experimentally and analytically.^(1,2) This relationship takes the form of

$$y = \frac{f}{E} Ac^n ,$$

where

y = crosshead extension

f = applied load

E = Young's modulus

c = crack length

A, n = Geometric constants.

From these results, the stress intensity coefficient K_I was determined as a function of load and extension for all specimen geometries.

(a) This paper is based on work performed under the U.S. Atomic Energy Commission Contract AT(45-1)-1830 - 1831

Subcritical-crack-growth tests were performed by loading the DCB specimen to a value of K_I somewhat lower than K_{IC} of the material. The crosshead was then stopped to maintain a fixed value of the displacement at the loading pins, or fixed extension, y . Slow crack propagation thus reduced the load necessary to maintain this value of extension, y . The crack length was monitored by recording the load applied to the specimen. From the above compliance relationship for constant y , the rate of crack propagation is

$$\frac{dc}{dt} = -\frac{1}{n} \left(\frac{Ey}{A}\right)^{1/n} f^{-\frac{(n+1)}{n}} \frac{df}{dt} .$$

Thus, the crack-growth rate was calculated by measuring the load decay rate

$$\left(\frac{df}{dt}\right).$$

Figure 2 shows the results of these tests on fully hardened D2 tool steel containing approximately 2 ppm hydrogen and tested in relatively humid air. The logarithm of the crack velocity, C , is shown as a function of the stress intensity parameter, K , for several test temperatures. Assuming that an Arrhenius relationship would describe the variation of crack velocity with temperature for a given stress intensity, an activation energy of approximately 10 Kcal/mole was determined. These results are shown in Figure 3.

We have found that, in all cases of subcritical crack growth which we have observed, the presence of small amounts of hydrogen and sufficiently high stresses at the crack tip (which are brought about by a high yield strength and a certain degree of stress triaxiality) are necessary to cause significant cracking rates.

The effect of liquid organic environments on the subcritical cracking rate of D2 tool steel at room temperature is shown in Figure 4. The material in these studies is the same as that referred to in Figure 2. In all cases, the specimen was loaded until cracking progressed in air and then the solutions were applied to the crack tip with an eyeglass. Capillary action held the solution in the side grooves of the specimen and around the crack tip. Referring to Figure 4, it may be seen that ethanol produced an order of magnitude increase in the crack propagation rate over that which occurs in air. Benzene produced a very interesting sharp increase in the stress dependence of the crack-growth rate which will be discussed later.

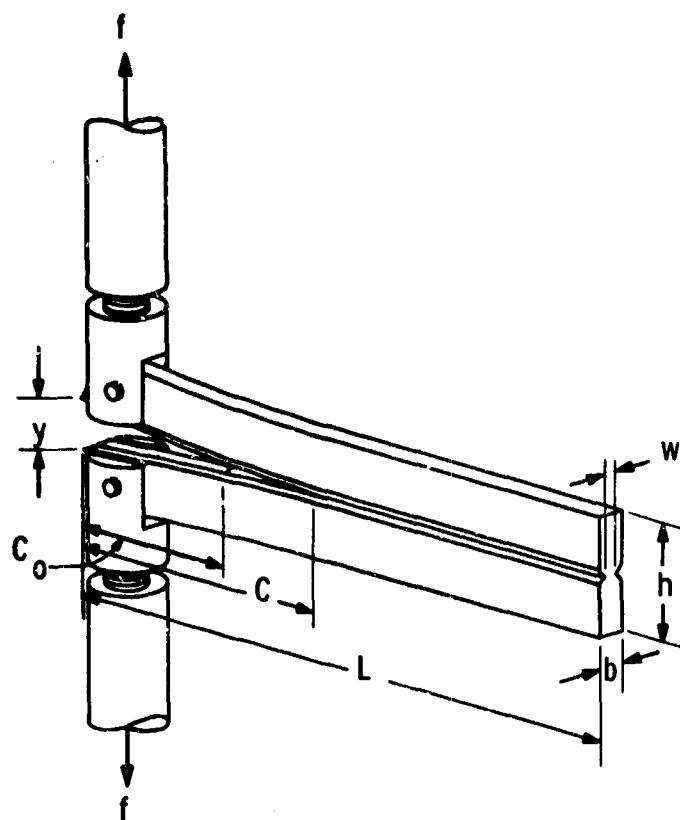


FIGURE 1. DCB SPECIMEN AND LOADING ARRANGEMENT

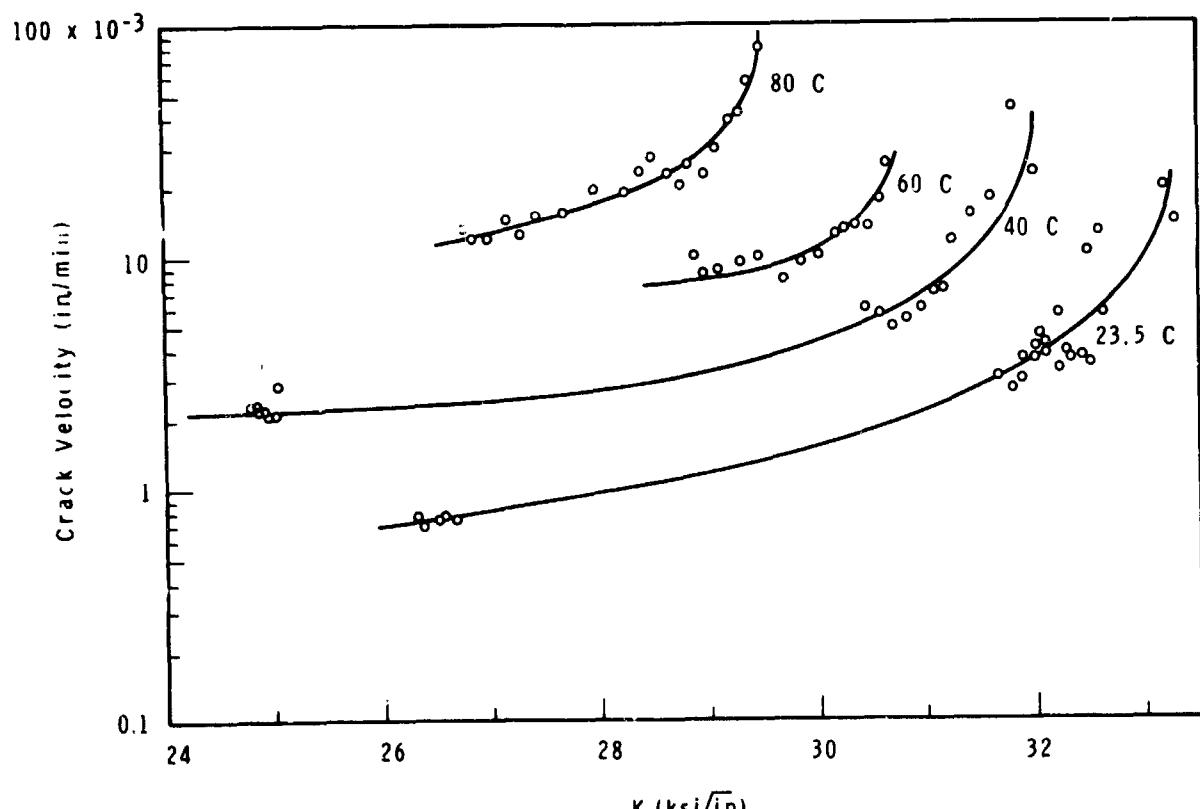


FIGURE 2. CONTINUOUS CRACK GROWTH OF FULLY HARDENED D2 TOOL STEEL CONTAINING 2 ppm HYDROGEN AND TESTED IN AN AIR ENVIRONMENT (RELATIVE HUMIDITY ~ 80%) AS INFLUENCED BY STRESS INTENSITY AND TEMPERATURE

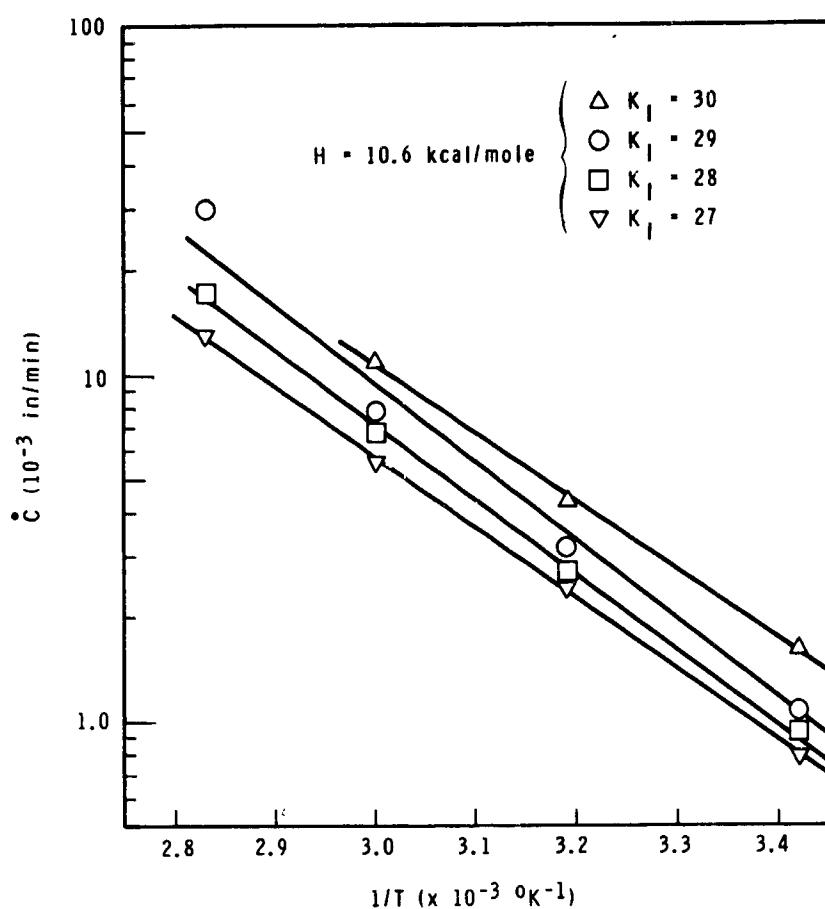


FIGURE 3. ACTIVATION ENERGY DETERMINATION FOR SUBCRITICAL GROWTH IN D-2 TOOL STEEL

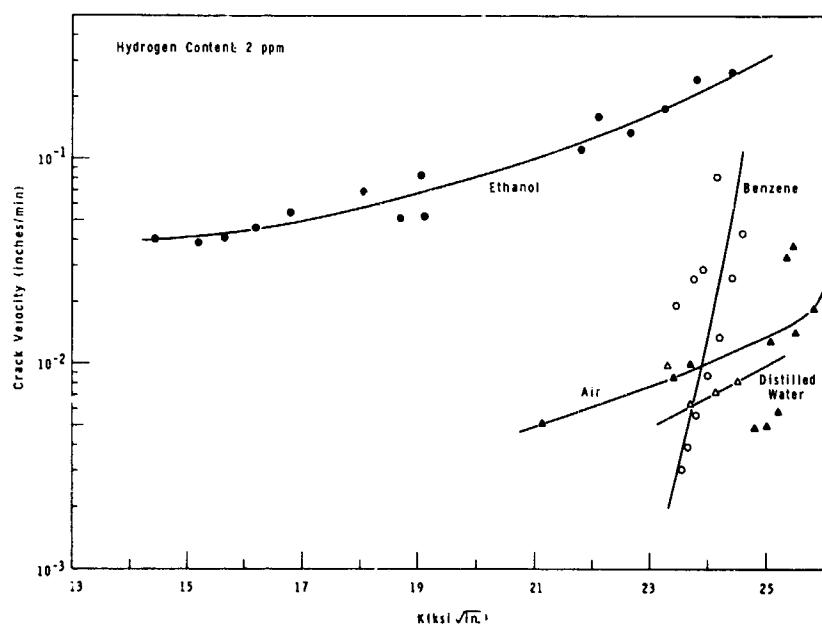


FIGURE 4. SUBCRITICAL CRACKING IN D2 TOOL STEEL IN AIR AND ORGANIC ENVIRONMENTS AT ROOM TEMPERATURE

REFERENCES

Figure 5 is a similar plot of the crack velocity as a function of K for Ti-6Al-6V-2Sn. This titanium alloy has an alpha-beta structure and approximately 180 to 190 ksi yield strength after heat treatment. The material was solution treated at 1650 F in argon for 1 hour, water quenched, then aged 6 hours at 1050 F before machining. The Rockwell hardness of the plate was R_C 44 to 45.

In comparing Figure 5 with Figure 4, it can be seen that the stress dependence of the crack-growth process in the 6-6-2 titanium is much greater for all environments than it was for the D2 tool steel. Again in comparing methanol and ethanol with the data taken in air, the stress dependence is similar, but benzene appears to cause very sharp increase in the rate of subcritical cracking above a stress level of 18 ksi $\sqrt{\text{in.}}$. Because of this similarity with the data obtained in high-strength D2 tool steel, the author is tempted to compare these results in light of similar mechanisms involving the embrittling effect of hydrogen at the crack tip and its thermally activated nature. No firm conclusion can be made at this point, but it is felt that these similarities justify further work in this area.

As pointed out earlier by many speakers at this meeting, the purity of the organic environments and knowledge of the amount and types of impurities in the system is important. The author agrees with these observations since it is plausible that even at very low levels contamination of the environment may produce significant changes in the crack-propagation rates of structural materials, including titanium alloys. It is for this reason that Battelle-Northwest has developed an ultrahigh-vacuum fracture test chamber. This equipment provides the capability for sensitive gas analysis. A liquid environmental facility is also being developed. It is felt that the mechanisms by which the external environment affects the rate of subcritical crack propagation can only be determined by resorting to sophisticated environmental purity control.

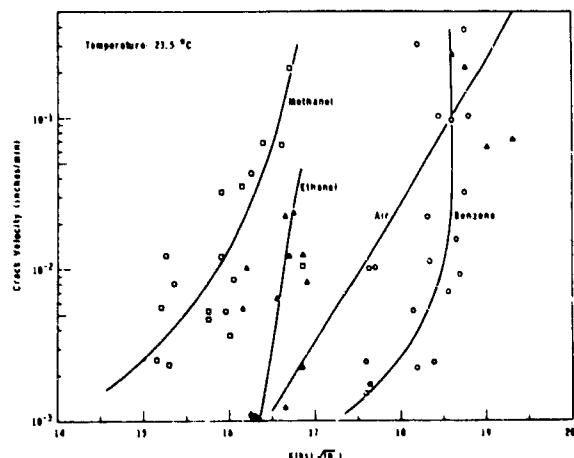


FIGURE 5. SUBCRITICAL CRACKING OF Ti-6Al-6V-2Sn IN ORGANIC ENVIRONMENTS

- (1) R. G. Hoagland, "On The Use of The Double Cantilever Beam Specimen For Determining the Plane Strain Fracture Toughness of Metals". (To be published in the ASME Journal of Basic Engineering, September, 1967).
- (2) Quarterly Progress Report: Irradiation Effects on Reactor Structural Materials, August, September, October, 1966. BNWL-CC-883, Edited at Pacific Northwest Laboratory November 15, 1966.

SIMILARITIES OF TITANIUM STRESS CORROSION
CRACKING PROCESSES IN SALT WATER AND
IN CARBON TETRACHLORIDE

by

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(Presented by Dr. K. E. Weber)

Several years ago it became evident that certain titanium alloys suffered a loss in notch toughness when brought in contact with salt water. The aqueous cracking problem prompted the investigation of the effects of other common substances on the room-temperature notch sensitivity of these alloys.

The test specimens used in these studies were three-point loaded notch toughness samples of the type specified in Reference 1. Before being tested, the samples were notched and subjected to cyclic loading until a uniform fatigue crack approximately 0.005 inch deep was produced at the tip of the milled notch. During testing, these specimens were dead-weight loaded to about 80 percent of the air failure stress, and the liquid being evaluated was placed in the notch by means of a hypodermic syringe. Crack progression was monitored by viewing the edge of the sample with a microscope and recording the crack growth sequence on 16-mm motion picture film. The basic test specimen utilized in this investigation is shown in Figure 1. The region of the sample viewed under the microscope is clearly indicated. A magnification of 10X (on the 16-mm film) and a film transport speed of 12 frames per second were used. The specimen was illuminated by means of a through-the-lens xenon arc lighting system.

Tests were run on Ti-8Al-1Mo-1V alloy using the techniques and equipment described above. It was soon discovered that pure carbon tetrachloride was also capable of producing room-temperature stress-corrosion cracks in this material. This result is shown in Figure 2, a and b, which are photographic sequences extracted from motion picture films of failures in salt water and in carbon tetrachloride, respectively. Notice in each case that the stress-corrosion fracture* initiated at the fatigue precrack (at the apex of the notch) and progressed off in either direction at approximately 45° to the applied stress. The general appearance of the crack growth patterns are essentially the same in both liquids. Postfailure microscopic examination of the specimens revealed that there were no visible

* The dark regions seen on these photos are not cracks but are indented regions caused by the formation of the stress-corrosion crack beneath. These regions appear black since the normal incidence light used to illuminate the samples is reflected off at an angle by the tilted metal surface and lost from the system.

differences in the fracture surfaces produced in these two solvent systems. Fatigue cracks and ductile fast fracture cracks in these specimens proceeded in a direction at about 90° to the applied stress, whereas the stress-corrosion cracks generally formed at 45° to the stress direction. At 80 percent of the air failure load, failure times of about 3 minutes were observed in both carbon tetrachloride and 5 percent salt water. Interestingly enough, notched samples without fatigue cracks did not form stress-corrosion cracks in either solvent.

In addition to crack morphology and failure time, there are other similarities in the stress corrosion cracking processes in salt water and carbon tetrachloride. The most interesting similarity is the composition of the corrosion products which form in these solvents. For example, spectrophotometric examination of both liquids withdrawn from typical stress-corrosion cracks revealed that corrosion products were present that displayed typical absorption peaks in the 2600 Å to 2800 Å region of the ultraviolet spectrum. The absorption curves for the products in these two solvents are shown in Figure 3. Notice that the corrosion products in carbon tetrachloride have an absorption peak at 2800 Å (curve I of Figure 3) whereas the products in salt water display a peak at 2640 Å (Curve II of Figure 3). It was discovered that when the carbon tetrachloride corrodent was brought in contact with water, some of the corrosion products diffused out of the carbon tetrachloride phase into the aqueous phase. When the water phase was extracted from the mixture and analyzed spectrophotometrically, it displayed the same optical absorption characteristics as Curve II. Conversely, when saltwater corrodents were withdrawn from cracks and extracted with pure carbon tetrachloride some of the corrosion products were transferred from the aqueous phase into the carbon tetrachloride. This resulting carbon tetrachloride phase then displayed the same absorption behavior as Curve I. These spectral data indicate that the final corrosion products which form in both carbon tetrachloride and salt water are essentially the same. These products are soluble in either liquid, although the optical absorption behavior of the products changes somewhat when they are transferred from one solvent to the other. This alteration in absorption characteristics may be a result of shifts in electronic structure that occur when the products dissolve in the two physically different solvent systems.

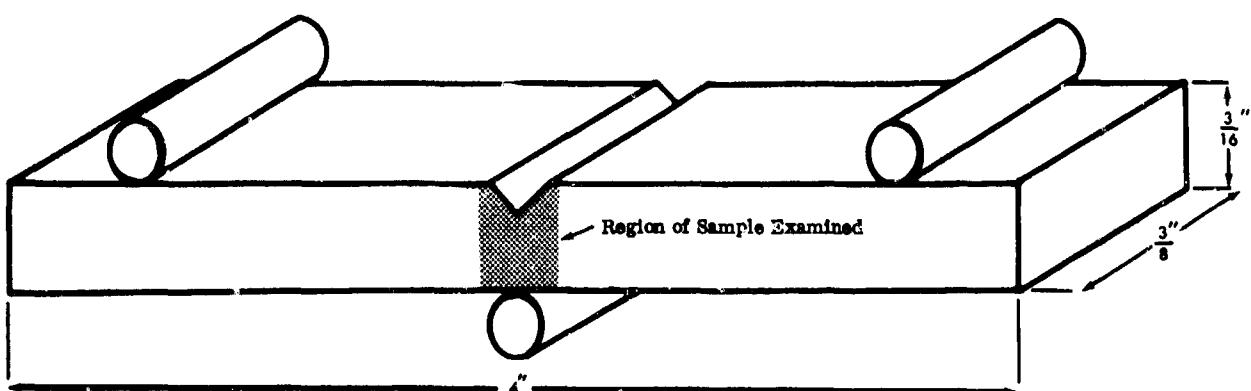


FIGURE 1. NOTCH TOUGHNESS SPECIMEN USED



a. 5% Salt Water



b. Carbon Tetrachloride

FIGURE 2. PHOTOGRAPHIC SEQUENCES
OF STRESS-CORROSION CRACK PRO-
GRESSION ON THE Ti-8Al-1Mo-1V
ALLOY

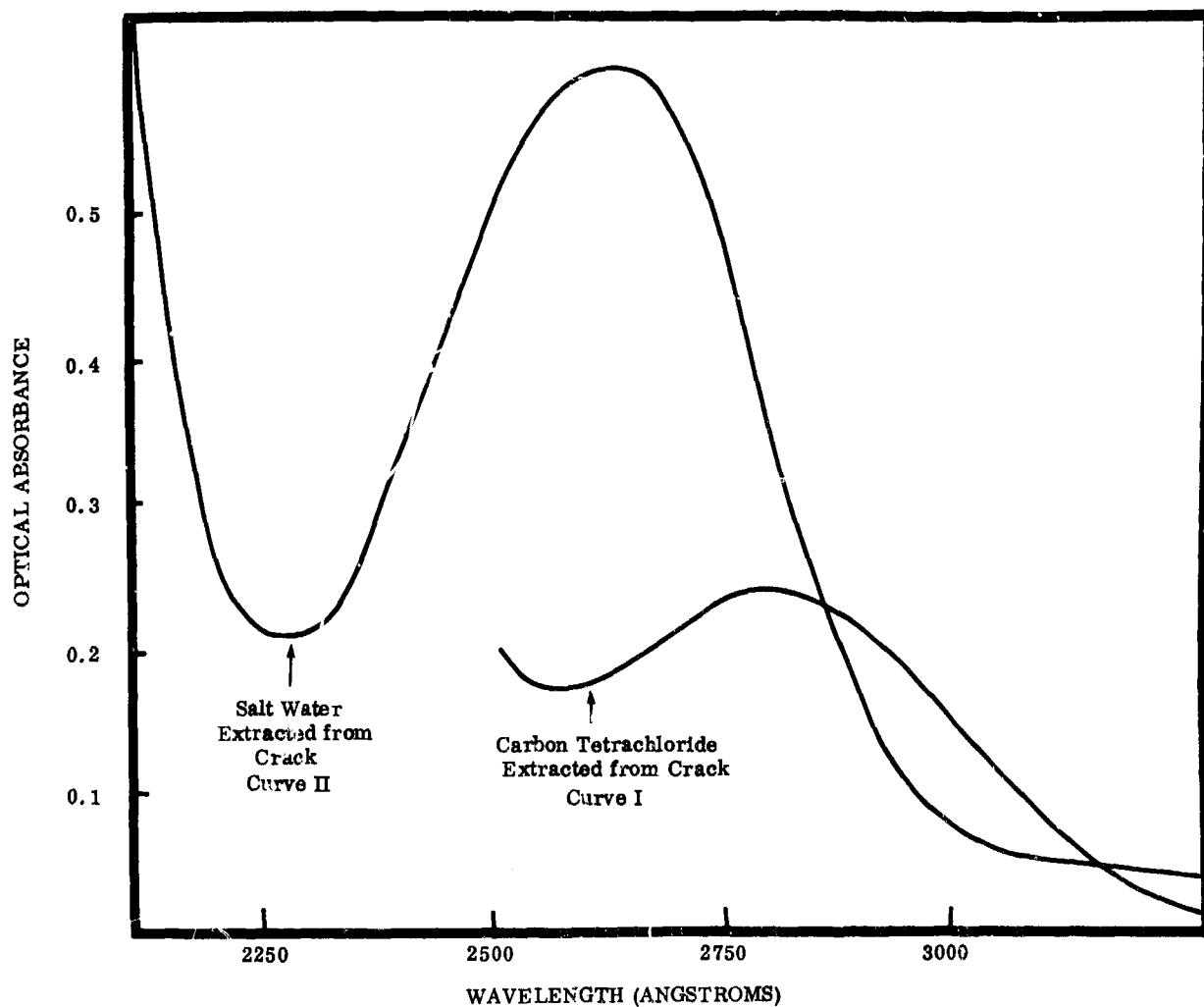


FIGURE 3. OPTICAL ABSORBANCE SPECTRA OF Ti-8Al-1Mo-1V CORROSION PRODUCT

REFERENCE

At this point, the fact that there are strong similarities in the cracking processes in these two solvent systems is evident. A brief summary of the likenesses of the cracking processes in these liquids is given below:

- (1) Crack direction, fracture surfaces, and general crack morphology are similar for specimens tested in these two liquids.
- (2) In both cases a precrack is required to initiate the stress-corrosion process.
- (3) For the same load conditions the cracking rate in CCl_4 and 5 percent salt water are comparable.
- (4) The corrosion products that form appear to be similar for both solvents.

Thus, in view of these observations, it may be concluded for the Ti-8Al-1Mo-1V alloy that stress-corrosion cracking in both carbon tetrachloride and saltwater corrodents are closely related processes.

During the course of this investigation, there were a number of interesting but isolated facts discovered concerning titanium alloy cracking in carbon tetrachloride. These facts may be of interest to the reader and are summarized below:

- (1) Addition of hydrocarbons containing olefinic double bonds retarded crack growth.
- (2) Addition of pure bromine or chlorine tended to inhibit cracking.
- (3) Addition or removal of moisture had no effect on the cracking rate.
- (4) Addition or removal of traces of hydrogen chloride produced no noticeable effect.
- (5) Washing the carbon tetrachloride with sodium thiosulfate solution (to remove traces of residual chlorine) produced no observable effects.

1. Campbell, J. E., Current Methods of Fracture Toughness Testing of High-Strength Alloys with Emphasis on Plane Strain, by Battelle Memorial Institute, Defense Metals Information Center, Report 207 August 31, 1964.

FRACTURE BEHAVIOR OF TITANIUM ALLOYS IN METHANOL ENVIRONMENTS

by

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INTRODUCTION

Preliminary results obtained in a mechanistic investigation* of the environment-sensitive mechanical behavior of alpha titanium alloys in methanol environments are presented. The investigation was commenced in February, 1966, after Mori et al. (1) published their observations of embrittlement of titanium by methanol solutions containing small amounts of HCl and H₂SO₄.

The present work has shown that embrittlement of titanium is not confined to methanol solutions containing nonoxidizing acids, but can be obtained in a wide variety of methanol environments including methanol vapor-dry air atmospheres.

ALLOYS AND TESTING PROCEDURES

The studies were confined to ELI (extra low interstitial) Ti-5Al-2.5Sn alloy, a series of titanium-aluminum binary alloys, and unalloyed A55 titanium. The alloys were initially in the form of 0.040-inch-thick sheet, except for the A55 material, which was obtained in the form of 0.020-inch-thick sheet. These materials had been hot rolled, sandblasted, pickled to remove 0.010 in., and vacuum annealed; the test pieces for the study of environmental factors were prepared from the sheet material in this condition. Both U-bend and tensile specimens (unnotched) were used in the environmental studies. The fasteners used to constrain the U-bend specimens were made, in each case, from the same alloy as that being tested, and during exposure the specimens and the environment were held in sealed containers. In the environmental tensile tests the specimen grips were so arranged as to be outside the environment container. Unless stated otherwise, the solutions used in environmental testing were prepared from reagent-grade methanol and other materials of highest purity available commercially. All compositions of solution are stated as percent by weight.

STUDIES OF CRACKING IN LIQUID METHANOL SOLUTIONSEnvironmental Factors

The initial stages of the investigation were concerned with repeating some of the experiments described by Mori et al. (1). A55 unalloyed titanium was selected for study at this stage of investigation, primarily because it closely resembled the material used by Mori et al. The results obtained (Table 1) confirmed their ob-

servations of (1) stress-corrosion cracking in methanol solutions containing HCl and H₂SO₄, (2) inhibition of cracking on increasing the water content of the acidic methanol solutions, and (3) absence of cracking in reagent-grade methanol. It was also found that the water content required for inhibition of cracking is to some extent dependent on the HCl content (Table 1).

Further studies using ELI Ti-5Al-2.5Sn alloy specimens and NaCl instead of HCl as the solute (Table 2) revealed that additions of the chloride as the sodium salt also gave rise to failures. Furthermore, it was found that embrittlement was not confined to methanol-chloride solutions, but occurred also in the presence of bromine and iodine, irrespective of whether these were added as the purified elements or as sodium salts (Table 2). Additions of fluorine to the methanol as HF did not cause embrittlement, although in solutions containing NaF surface cracking was in evidence after an exposure of 2 weeks.

The possibility that inhibition of cracking by additions of water (Table 1) is the result of a competitive adsorption of water and halogens and that methanol acts merely as a carrier, was investigated using chloride solutions of dimethyl sulfoxide (DMSO). It has been shown that DMSO will solvate and shield only the cations, leaving the anions (e.g. chloride ions) free to react (2). Because of the low solubility of NaCl in DMSO, LiCl was used as the solute. The results obtained using DMSO solutions are shown in Table 3, where it is seen that stress-corrosion cracking does not occur in DMSO containing substantial quantities of chloride introduced either as LiCl or HCl. It is also shown (Table 3) that dilution of methanol-HCl solutions with DMSO does not inhibit cracking, except at very low methanol contents. The data obtained using DMSO solutions indicate that the function of methanol is more than to provide a carrier for halogens or other reactive species, and that it enters into the reaction leading to cracking.

This conclusion led to consideration of the possibility that pure methanol by itself would lead to cracking. Since no failures had been obtained in A55 titanium (Table 1), tests were extended to ELI Ti-5Al-2.5Sn alloy specimens. Results obtained by exposing these alloy specimens to various methanol environments are shown in Table 4, where it is seen that methanol liquid treated to remove traces of water (which may be picked up on exposure to the atmosphere) causes

* Current investigation by A. J. Sedriks, P. W. Slattery, and E. N. Pugh.

TABLE 1. RESULTS OBTAINED WITH UNALLOYED TITANIUM (A55) U-BEND SPECIMENS

Environment	Time to Failure
CH_3OH (reagent grade)	N.F.
H_2O (distilled)	N.F.
H_2O (distilled) + 0.59% HCl	N.F.
$\text{CH}_3\text{OH} + 0.59\% \text{HCl} + 1.01\% \text{H}_2\text{O}$	2 hours
$\text{CH}_3\text{OH} + 0.59\% \text{HCl} + 1.14\% \text{H}_2\text{O}$	6 days
$\text{CH}_3\text{OH} + 0.59\% \text{HCl} + 1.45\% \text{H}_2\text{O}$	N.F.
$\text{CH}_3\text{OH} + 0.45\% \text{H}_2\text{SO}_4 + 0.001\% \text{H}_2\text{O}$	7 days
$\text{CH}_3\text{OH} + 0.55\% \text{HCl} + 0.94\% \text{H}_2\text{O}$	1 hour
$\text{CH}_3\text{OH} + 1.10\% \text{HCl} + 1.88\% \text{H}_2\text{O}$	2 days
$\text{CH}_3\text{OH} + 1.65\% \text{HCl} + 2.82\% \text{H}_2\text{O}$	N.F.

N.F. = No failure after 6 months of exposure

TABLE 2. RESULTS OBTAINED WITH ELI Ti-5Al-2.5Sn ALLOY U-BEND SPECIMENS

Environment	Time to Failure
$\text{CH}_3\text{OH} + 0.59\% \text{HCl} + 1.01\% \text{H}_2\text{O}$	1 day
$\text{CH}_3\text{OH} + 0.35\% \text{Br}_2$ (a)	30 min.
$\text{CH}_3\text{OH} + 3.5\% \text{Br}_2$ (a)	hours
$\text{CH}_3\text{OH} + 0.012\% \text{I}_2$ (a)	2 days
$\text{CH}_3\text{OH} + 1.35\% \text{I}_2$ (a)	5 hours
$\text{CH}_3\text{OH} + 0.75\% \text{HF} + 0.75\% \text{H}_2\text{O}$	N.F. (2 months)
$\text{CH}_3\text{OH} + 0.074\% \text{NaCl}$	2 days
$\text{CH}_3\text{OH} + 0.129\% \text{NaBr}$ (b)	2 days
$\text{CH}_3\text{OH} + 0.188\% \text{NaI}$ (b)	7 days
$\text{CH}_3\text{OH} + 0.053\% \text{NaF}$ (b)	2 weeks (c)

(a) Bromine and iodine added as purified liquid and solid, respectively.

(b) Data unavailable at time of Seminar-added in proof.

(c) Surface cracking only.

TABLE 3. RESULTS OBTAINED WITH UNALLOYED TITANIUM (A55) U-BEND SPECIMENS

Environment	Time to Failure
DMSO + 1% LiCl	N.F.
DMSO + 3% LiCl	N.F.
DMSO + 10% LiCl	N.F.
DMSO + 0.43% HCl + 0.73% H_2O	N.F.
DMSO + 73.23% $\text{CH}_3\text{OH} + 0.55\% \text{HCl} + 94\% \text{H}_2\text{O}$	22 hours
DMSO + 41.44% $\text{CH}_3\text{OH} + 0.48\% \text{HCl} + 0.84\% \text{H}_2\text{O}$	1 day
DMSO + 15.13% $\text{CH}_3\text{OH} + 0.45\% \text{HCl} + 0.78\% \text{H}_2\text{O}$	28 days
DMSO + 0.76% $\text{CH}_3\text{OH} + 0.43\% \text{HCl} + 0.73\% \text{H}_2\text{O}$	N.F.

N.F. = No failure after 6 months of exposure.

TABLE 4. RESULTS OBTAINED WITH ELI Ti-5Al-2.5Sn ALLOY U-BEND SPECIMENS

Environment	Time to Failure
CH_3OH (reagent grade 99.9 mol % pure)	8 days (a)
CH_3OH (reagent grade, dried with CaO powder)	4 days (a)
CH_3OH (reagent grade, redistilled)	2 days (a)
CH_3OH vapor - dry air mixture	1 day (min.)

(a) Data added in proof.

rapid embrittlement. No chloride could be detected in the liquid methanol by the silver nitrate test.

Metallurgical Factors

The only metallurgical variable that has been studied to date is the aluminum content of Ti-Al binary alloys. The equilibrium diagram of the titanium-aluminum system, as determined by Crossley⁽³⁾, is shown in Figure 1. Alloys containing 0 to 7.5 weight percent Al were studied, and it should be noted (Figure 1) that on slow cooling from temperatures in the alpha range precipitation of Ti_3Al is possible at aluminum contents in excess of 4.5 weight percent. With respect to Ti_3Al , Lane⁽⁴⁾ has found that binary Ti-Al alloys of a composition within the $\alpha + Ti_3Al$ phase region, heat treated to produce Ti_3Al , show susceptibility to accelerated crack propagation in seawater, whereas alloys with a lower aluminum content are not susceptible. Accordingly, it was decided to determine whether a similar dependence of susceptibility on aluminum content existed in methanol solutions. The results obtained using U-bend specimens, prepared from binary Ti-Al sheet alloys that had been vacuum annealed at 850°C and slowly cooled in the vacuum furnace to room temperature, are shown in Table 5. These show that cracking may be obtained in both pure titanium and Ti-2 weight percent Al in methanol solutions containing bromine and iodine. Consequently, the presence of Ti_3Al does not seem to be a requirement for embrittlement to occur. Increasing the aluminum content does, however, increase susceptibility to cracking. This increase is better demonstrated in Figure 2, which shows data obtained in constant-load tensile test in methanol-HCl solutions using binary Ti-Al alloys containing 3, 5, and 7 weight percent Al. No data are yet available on tests of pure titanium or Ti-2 weight percent Al alloy.

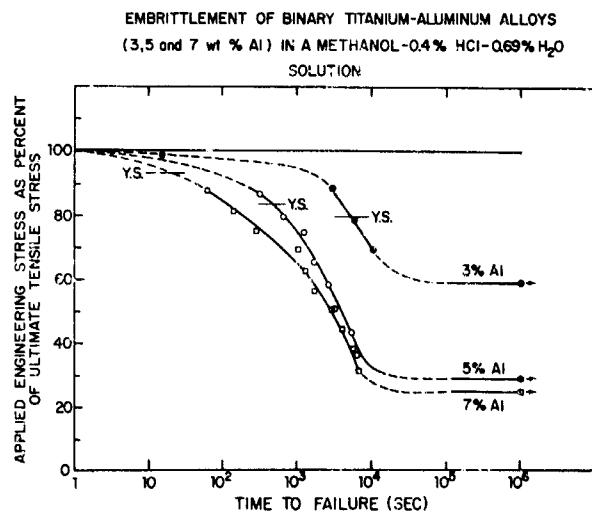


FIGURE 2.

STUDIES OF CRACKING IN METHANOL VAPOR-AIR ATMOSPHERES

As indicated in Table 4, embrittlement of titanium alloys was also obtained in methanol vapor-dry air atmospheres. These tests were carried out by placing U-bend specimens within the vapor space of a closed dessicator (volume = 2000 cc) partially filled with reagent-grade methanol that contained a suspension of CaO dessicant. A dessicant tray was also placed in the vapor space. The tests were carried out at room temperature (72°F).

Cracking was observed in U-bend specimens of the ELI Ti-5Al-2.5Sn alloy, A55 unalloyed titanium, and Ti-7.5 weight percent binary alloy. Times to failure varied between 1 day and 3 weeks. Ambrose and Kruger⁽⁵⁾ have found that the volume of vapor is important in such tests, and that at small volumes both the time to failure and the extent of scatter is reduced.

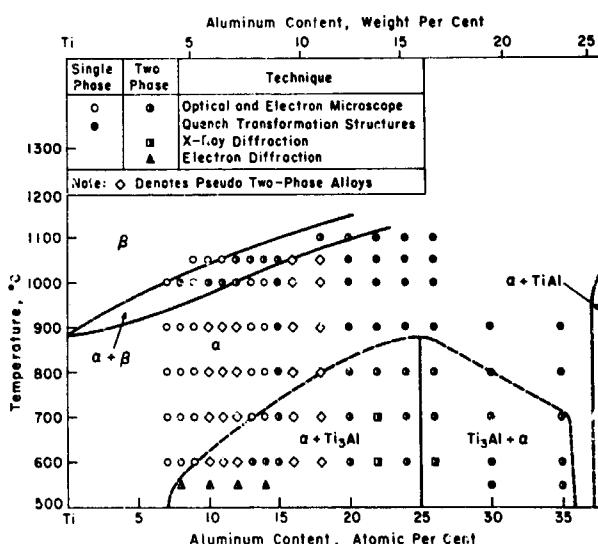


FIGURE 1. BINARY Ti-Al PHASE DIAGRAM, AFTER CROSSLEY⁽³⁾

TABLE 5. RESULTS OBTAINED WITH BINARY Ti-Al ALLOY U-BEND SPECIMENS

Environment	Alloy	Time to Failure
$\text{CH}_3\text{OH} + 0.59\% \text{HCl} + 1.01\% \text{H}_2\text{O}$	Ti	F. (a)
	Ti-2% Al	F. (a)
	Ti-5% Al	4 days
	Ti-7.5% Al	2 hours
$\text{CH}_3\text{OH} + 0.35\% \text{Br}_2$	Ti	3 days
	Ti-2% Al	3 days
	Ti-5% Al	2 hours
	Ti-7.5% Al	30 min.
$\text{CH}_3\text{OH} + 1.25\% \text{I}_2$	Ti	F. (a)
	Ti-2% Al	F. (a)
	Ti-5% Al	30 min.
	Ti-7.5% Al	20 min.
$\text{CH}_3\text{OH} + 0.12\% \text{I}_2$	Ti	2 weeks
	Ti-2% Al	2 weeks
	Ti-5% Al	2 hours
	Ti-7.5% Al	2 hours

(a) Failed by intergranular corrosion after exposure for 1 month.

U-bend specimens of pure titanium, Ti-2 weight percent Al, and Ti-5 weight percent Al alloys did not show cracks on exposure up to 1 month. However, examination of surfaces of these U-bend specimens after exposure revealed stains or discolored areas which developed cracks on further straining in air. The cracking was localized to the stains. Similar stains were observed to form on unstressed specimens of pure titanium during exposure to methanol vapor, and on subsequent straining these specimens also formed cracks associated with the stains. This type of embrittlement could be eliminated by vacuum annealing the exposed specimens at 320°C for 4 hours at 10⁻⁶ mm Hg.

DISCUSSION OF POSSIBLE MECHANISMS OF EMBRITTLEMENT

Liquid Methanol Solutions

Tomashev et al.⁽⁶⁾ have shown that the nature of the corrosive attack on unstressed alpha titanium in methanol bromine solutions changes from general surface dissolution to intergranular attack as the bromine content is reduced from 5 to 1 percent. They also report that the attack can be inhibited by cathodic polarization, and reduced and ultimately stopped by increasing the water content of the methanol-bromine solution.

The localization of attack with decreasing bromine content was also observed in the present investigation using stressed specimens. It can be seen from Table 2 that the time to failure is reduced by an order of magnitude as the bromine content is decreased from 3.5 to 0.35 percent. Specimens exposed to 3.5 percent bromine solution showed attack along many grain boundaries as well as pronounced general surface attack. Specimens exposed to 0.35 percent bromine solution failed by the intergranular propagation of a single crack, and general surface attack was very little in evidence. The similarity between the corrosion of stressed and unstressed specimens would tend to suggest that the mechanism by which cracks propagate during exposure to methanol-bromine solutions involves localized anodic dissolution.

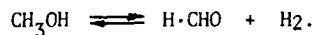
At the present stage of the current investigation there is insufficient evidence to show whether anodic dissolution is also associated with other methanol liquid solution environments. Conditions leading to failures in apparently pure and water-free methanol liquid (Table 4) must be carefully examined and the exact role of the halogens determined before any specific mechanism can be suggested.

With regard to metallurgical factors, results obtained to date have eliminated the requirement of Ti_3Al for embrittlement to occur in Ti-Al alloys in methanol-halogen solutions. Consequently, consideration must be given to other effects that arise from the introduction of aluminum atoms in the alpha titanium lattice. One of the effects is the change in dislocation distribution on deformation with increasing aluminum content. In this respect, Blackburn⁽⁷⁾ has shown that in binary Ti-Al alloys, the dislocation distribution changes from cellular to coplanar as the aluminum content is increased in the range 0 to 9 weight percent Al. It could be argued, therefore, that the present data show a distinct correlation between susceptibility to cracking in methanol-halogen solutions with increasing coplanarity of dislocation distribution. The correlation could be rationalized by postulating that increasing coplanarity reflects an increasing tendency to concentrate stress at a crack tip.

Any correlation between dislocation distribution and susceptibility to cracking may not be particularly significant without knowledge of changes in the structure and passivity of the surface films with increasing aluminum content. For instance, Andreeva and Kazarin⁽⁸⁾ have determined the polarization curves for titanium and Ti-Al binary alloys in aqueous hydrochloric and sulfuric acids, and their data may be interpreted as showing that the presence of aluminum in the alpha titanium lattice lowers the protectiveness of the surface film. Clearly, the effect of aluminum content on the structure and passivity of surface films formed in methanol-halogen solutions must be established before any convincing rationalization of the effect of aluminum can be made.

Methanol in Vapor-Dry Air Environments

The possibility that some form of hydrogen embrittlement is responsible for failures in the presence of methanol vapor was suggested by Ambrose and Kruger.⁽⁵⁾ The present observations that it is possible to embrittle unstressed titanium merely by exposure to methanol vapor and to eliminate this embrittlement by vacuum annealing would tend to confirm this suggestion. The possibility exists that hydrogen may be generated by the well-known vapor-phase reaction:



This reaction is known to occur at elevated temperatures (300 C) when methanol vapor is passed over Cu, Cu-Cr, Cu-Ni, or Ag catalysts. In the presence of air, the hydrogen usually combines to form water. Clearly, it is necessary to establish whether this reaction can occur at room temperature in the presence of titanium containing an air-formed surface film. It should also be noted that further oxidation of the aldehyde to formic acid may also be possible, and that titanium exhibits "border-line" passivity in formic acid.^(9,10)

CONCLUSIONS

- (1) Titanium and alpha titanium alloys exhibit embrittlement when exposed to
 - (1) liquid methanol solutions containing small quantities of halogens,
 - (2) water-free methanol liquid, and
 - (3) in methanol vapor-dry air atmospheres.
- (2) In methanol vapor-dry air atmospheres the simultaneous application of stress and exposure to the environment is not necessary to cause embrittlement.
- (3) Embrittlement in liquid methanol solutions can be inhibited by increasing the water content of the solution.
- (4) Increase in the aluminum content of binary Ti-Al alloys increases susceptibility to embrittlement.
- (5) The results obtained to date are consistent with the possibility that in methanol-bromine solutions cracking involves localized anodic dissolution, while in methanol vapor-dry air atmospheres, the possibility of some form of hydrogen-induced embrittlement cannot be ruled out.

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MECHANISM OF TITANIUM FAILURE

by

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Martin Marietta has been in the high-pressure titanium vessel business for approximately 10 years without yet having had a failure. The Titan I, you may remember, had high-pressure helium in a titanium sphere inside the LOX tank. We have five high-pressure titanium vessels in the transtage of Titan IIIC, two containing propellants, two containing helium, and one containing nitrogen.

Eighteen months ago, the Air Force questioned the marginality of titanium tanks built by Martin Marietta's Denver Division for use with green or white nitrogen tetroxide. To answer this question, we started a program to determine whether or not we could permit the use of the so-called white nitrogen tetroxide in our titanium tanks, while maintaining high reliability. We have concluded from these studies that we cannot, for whenever the white nitrogen tetroxide is used with stressed titanium, failure occurs.

I would like to give you the background on what we believe is happening regarding titanium stress corrosion. The Allied Chemical Company made nitrogen tetroxide (N_2O_4) by oxidizing nitrosyl chloride ($NOCl$) to produce nitryl chloride (NO_2Cl). The nitryl chloride was then fractionally distilled to separate chlorine and NO_2 . The NO_2 was cooled and the dimerized N_2O_4 was produced, with a trace of residual $NOCl$. The Hercules Powder Company also produces N_2O_4 . They oxidize ammonia to make nitric oxide (NO) that is further oxidized to NO_2 . The NO_2 is similarly cooled to produce N_2O_4 . The Hercules product contains some nitric oxide, NO , and a trace of $NOCl$. Now, NO is blue, NO_2 is brown, and N_2O_4 and $NOCl$ are colorless. Thus, at 60° F, the N_2O_4 from Allied looked brown, while the N_2O_4 from Hercules looked green-blue. In an attempt to control more closely the color of the product procured to one specification, it was decided to require that all nitrogen tetroxide be brown at room temperature. The excess nitric oxide in the Hercules product was oxygenated and the green color was dispelled. It was the advent of the "white" or oxygenated nitrogen tetroxide that led to the rash of failures of titanium as the result of stress corrosion.

We believe that the mechanism of attack is that of chlorine on base titanium:



The titanium tetrachloride formed is a liquid, and hence will go into solution in the oxidizer. The chlorine is produced by the oxygenative step; nitrosyl chloride is converted to NO_2 and Cl_2 , as in the Allied process, but the Cl_2 is not removed.

Now, the same general mechanism is not true for the fuel. Chlorine plus an amine like hydrazine will form a hydrochloride. This removes the active chlorine and the fuel does not attack stressed titanium.

Naturally, then, we believe that Cl_2 or some form thereof is causing stress corrosion. Furthermore, we think stress corrosion of titanium in methanol may occur similarly. We suspect that the methanol contains covalent hydrogen chloride and there are a number of indications in support of that. The book by F. A. Patton, Progress in Inorganic Chemistry, Vol 4, 1960, states that the reaction of titanium as a metal plus pure methanol does not occur. However, the reaction of titanium tetrachloride and methanol will produce tetramethoxy titanium and HCl . We think this is the basis by which methanol can produce stress corrosion. If one starts with titanium and a small amount of HCl in the dry methanol, as a chlorinating agent, one makes titanium tetrachloride and hydrogen. Once these constituents are present, reaction with methanol should produce the salt and hydrogen chloride. The HCl continues the corrosion reaction. Therefore, the reaction ought to be sustaining at whatever level of hydrogen chloride is initially present. I do not wish to exclude other sources of reactive chlorine atoms in methanol, but hydrogen chloride looks like the most probable one.

The electrochemical experiments previously described by Bob Johnson of MSC may be explained as follows. Hydrogen chloride is a polar molecule. One expects that hydrogen chloride would line up with the hydrogen near the negative electrode. Covalent chlorine would then be available to the positive electrode. When the positive electrode is stressed titanium, rapid corrosion results. When the polarity is reversed, chlorine seeks the unstressed electrode, and no reaction is observed. These results, obtained at MSC, indicate that both covalent chlorine and stressed titanium are needed for stress corrosion.

It has been established that stressed titanium plus dry methanol to which has been added some HCl is failure prone. Titanium plus methanol plus trace amounts of hydrogen chloride and water produces no reaction. This leads me to believe that ionic hydrogen chloride (aqueous) is not involved in this corrosion process; the rate is not a function of activity of the chloride ion. So I rule out chloride ion as being detrimental and conclude that chlorine atoms alone, afforded by chlorine or hydrogen chloride, as opposed to ionic hydrogen chloride, are the culprits.

DISCUSSION:

(A. W. Bauer,
E. I. du Pont,
de Nemours & Company, Inc.
Wilmington, Delaware)

This idea, of course, leads to the prediction that anything which can produce active chlorine atoms should be prevented from contacting titanium under stress. The general form of the equilibrium constant shows that certain species of Freon will contain a trace of Cl₂. You can write the thermodynamic equilibrium constant for the formation reaction and show that, however small, there ought to be some HCl or Cl₂ present. This idea led to our prediction that certain Freons might also be conducive to stress corrosion of titanium. This hypothesis has been borne out by recent experiments with Freon MF, CFCl₃. We believe according to the equilibrium constant that some chlorine is always present in solution. The corrosion reaction is accordingly self-sustaining as long as some Freon MF is present.

Incidentally, water with a high chlorine content and some chloride salts put through zeolite to achieve demineralization may produce stress corrosion rather than immunity. The chloride is removed, but the active chlorine may get through the zeolite. I really do not know that reaction well enough to be able to say. On the other hand, inhibited water affords good immunity. We use water inhibited with sodium chromate and we have not had any stress -corrosion difficulties as yet.

I would like to reiterate that the corrosion product according to our theory would be titanium tetrachloride, which is a liquid. Accordingly, a corroding tank is thought to be slowly dissolving much like was shown in the motion pictures presented by Dr. Weber.

Bob Johnson told us also about an experiment where corrosion was found. A titanium tank was filled with methanol, whose titanium concentration was found to be near zero. At the end of the test, a stress-corrosion failure had occurred and the titanium concentration in the liquid had risen by an order of magnitude. I would like to know more details; that is, (1) whether the titanium in the liquid were ionic or metallic, and (2) if it were titanium tetrachloride or titanium tetramethoxide.

The last thing I am a bit concerned about is whether or not the preparation of specimens at one time and their use some weeks later is tricking us. I would prefer to see an experiment designed much like Dr. Weber used where he produced the stress in the environment. Henry Heubusch of Bell Aerosystems also described a way to stress specimens in the actual test environment. Such procedures avoid stressing in air, and the resultant possibility of protection by oxygenation. If the specimens become oxidized, the titanium becomes less reactive to chlorination.

Finally, let me say that I have examined all of the data that have become available to us. We have yet to find any experiments that contradict our theory. At the same time, every experiment that we understand can be explained by this mechanism.

Needless to say I was quite interested to hear about the chlorine in Freon. Although I do not know much about the amount of chlorine in chlorinated solvents or in the chlorinated products produced by other suppliers, Du Pont does have a good bit of information about the chlorine content of our Freon TF and the Freon MF. There is no detectable chlorine in either one of these products.

Now, Jim, you mentioned forming the elemental chlorine and the equilibrium shifting and making more chlorine to replace that which was consumed in the process of cracking. Consider the formation of chlorine in the drum, starting with material as it left the plant (did not have any chlorine in it detectable by very sensitive tests.) Could the chlorine form in the product as it is stored or shipped around the country? Well, the reaction that takes place upon chlorides reverting back to the elemental materials requires a high temperature and a very active catalyst. Suppose that we actually had the materials in the drum and put the catalysts in to activate the reaction and heated the drum to several hundred degrees. What is the maximum amount of elemental chlorine that could be formed? Well, fortunately we have calculated these equilibrium contents. In Freon MF the maximum amount of chlorine which would form is half a microgram for a 55-gallon drum. In Freon TF only one-ten millionth of that concentration can form.

Now, I can see that the titanium may be extracting halogen atoms from the materials themselves, but I can not believe there is any free chlorine floating around in the liquid. I was particularly interested in discounting the reaction between the methanol and titanium. I am sure that if you take a piece of titanium that is relaxed and throw it in the methanol nothing is going to happen; this is not what we are dealing with here. All of the data I have seen today show that the dominant factor promoting stress corrosion of titanium is the applied stress. The more we stress titanium the faster the crack goes. Evidently, we are stressing the titanium bonds and lowering the activation energy. The free energy of forming the titanium methoxide is favorable but it requires a very high activation energy. Thus we are not dealing with the simple methanol-titanium reaction here. We are dealing with activated titanium where the bonds have been stretched, and the activation energy for this reaction has been significantly lowered. I find it quite conceivable that the titanium is extracting halogen from many of the halogenated materials and the rate of the reaction can depend on two things. One is the stress on the titanium, and the more stress you

have the lower the activation energy required; the other is the extractability of the halogen from the materials, the more stable the solvent the less likely is the titanium able to extract the halogen.

Also, I do not find inconsistent the possibility that the alcohols are reacting directly with titanium. If we look at the chemistry of the reactions of any series of alcohols with metals we see that titanium reacts pretty much in similar degrees. This is, in the methyl alcohol range, titanium and other metals are most reactive; in ethyl alcohols second most reactive, and so on down the line. This behavior is consistent with the information presented here.

I am sympathetic that you are trying to bring some rhyme and reason into this whole titanium stress-corrosion picture. However, Jim, I just do not see evidence of chlorine floating around in the liquid and consequently I can not believe that is the cause.

Reply by Dr. Bowman:

I, of course, have no evidence of chlorine. But, such must be the case or our proposed mechanism is wrong, which is quite possible; or it is possible that the amount of impurities in the Du Pont product, with all apologies to the Du Pont Company, might be significant. The Du Pont

Company was kind enough to tell us about the number and the concentration of impurities in Freon MF. I believe there were eight and certainly if you can detect those, it means they are in higher concentration than that of chlorine according to the equilibrium constant. I find no cause to investigate that myself. We, of course, have had no failures. As to the question of whether or not stressed titanium plus methyl alcohol will form titanium methoxide, I believe that Mori et al. said it would not. All I can do here is present their data.

A. Hurlich, General Dynamics/Convair,
San Diego, California

The data of Herrigel, Sedriks, and Lisagor and some tests we did at Convair appear to be quite consistent. We did some work in chloride-free, anhydrous methyl alcohol on some STA material that had been notched with the K_t of 6.3. The specimens were stressed for 22 days, the last 10 days at 92 percent of the yield (135 ksi) and had no fractures. But, when we added as little as 1/2 ppm of HCl to the methyl alcohol we got fractures in less than 24 hours. Thus, I quite agree with your statement that things that contain a smidgen of HCl can give the sustained reaction producing titanium tetrachloride which reacts to form a titanium alkoxide plus hydrochloric acid and further continues to produce failure of the titanium.

When you talk about 1/2 ppm of chloride, I think we have reestablished today what we have known in the past, that titanium is an extremely reactive material.

INVESTIGATION OF STRESS-CORROSION CRACKING OF TITANIUM ALLOYS*

by

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Our original interest in the stress cracking of titanium in methanol started with the Japanese work of Mori et al.⁽¹⁾ In this work, HCl or H₂SO₄ had been found to be a necessary addition for cracking to occur. Our thoughts on this problem were that other halogen compounds, e.g., NaCl, would probably yield similar results.

Existing apparatus for testing foil was found to be satisfactory for Ti-6Al-4V alloy that was 0.003 inch thick and 1/4 inch wide. The entire investigation discussed here was carried out with this alloy in the cold-rolled and annealed condition with a yield strength of 132,000 psi and an elongation of about 12 percent. The test specimens, cut to 4-inch lengths and cleaned with methyl ethyl ketone, were threaded through a 1-1/4-inch-diameter polyethylene bottle and sealed with epoxy before adding the methanol solution. Figure 1 shows a specimen under test (right) and another broken with the bottle removed (center). Specimens were stressed to 85 percent of yield strength in direct tension applied with dead weights.

It was found that as water was added to a high-purity methanol the susceptibility toward stress-corrosion cracking was first increased, then decreased with further additions. In other words, a minimum in the time to failure occurs. This indication of a minimum as a function of the water content was believed to support an electrochemical mechanism. Figure 2 shows the effects of adding 0.01N HCl and 0.01N NaCl to methanol. Note that the times to failure are quite similar in both of these solutions. There is a displacement, however, as to where the absolute minimum comes for these solutions as a function of percent water.

Thinking of this primarily in terms of an electrochemical mechanism, electrode potential measurements as a function of time were made, as plotted in Figure 3 for varying amounts of water added to the methanol. For 0.01N HCl, these go

progressively from 0.063 percent water on up to 100 percent water. Figure 4 shows the 1-hour values taken off the curves of Figure 3. Again, the reaction varies with the water content. An important aspect is that the two straight lines cross in the vicinity of 0.6 percent water and indicate where this minimum should occur. Figure 5 shows a summary of the data for the Ti-6Al-4V alloy. Note that 0.15N NaCl represents about the maximum amount of NaCl it is possible to dissolve in purer methanol. As you decrease the amount of NaCl in the methanol, the position of the minimum moves towards the lower water content and the minimum becomes less pronounced. With such narrow minimums as shown with the least NaCl added, it is almost impossible to locate the composition of the solutions necessary to obtain maximum susceptibility to stress corrosion cracking. It can be done, however, with electrode potential measurements as illustrated in Figures 2 and 4 discussed above and as shown for maraging steel.⁽²⁾

Another indication that the cracking is electrochemical as opposed to a hydrogen embrittlement mechanism is shown in Figure 6. The influence of cathodic and anodic polarization on the time to failure of the Ti-6Al-4V foil in a methanol-0.15N NaCl solution containing 0.3 percent water was examined. Anodic polarization decreased the time to failure while small cathodic current densities significantly increased the time to failure, which is consistent with a mechanism of corrosion along an active anodic path. It is not consistent with a mechanism of hydrogen embrittlement. At the highest cathodic current densities tested, hydrogen may be involved in the two failures obtained.

The mechanism is probably similar to that described for maraging steel foils, which exhibited a high susceptibility to stress corrosion cracking in aqueous solutions of 10-12 pH.⁽²⁾ It was possible to show some correspondence with the Pourbaix diagram for iron, but no such diagram is available for titanium-methanol system. The changing slopes of the electrode potential curves for the titanium alloy probably indicate changes in the surface films being formed with varying water contents in methanol.

* This work was supported in part by the National Aeronautics and Space Administration under Research Grant NGR-39-008-014.

(1) Mori, K., Takamura, A. and Shimose, T., "Stress Corrosion Cracking of Ti and Zr in HCl-Methanol Solutions", *Corrosion* 22, pp. 29-31 (February, 1966).

(2) Green, J. A. S. and Haney, E. G., "Relationships Between Electrochemical Measurements and Stress Corrosion Cracking of Maraging Steel", *Corrosion* 23, pp. 5-10 (January, 1967).

Passivation is probably occurring as the water content is increased. It does not occur completely at any definite value of electrode potential or water content in methanol-- rather it would occur over a short range of values. Within the range of water content where the minimum occurs, passivation is proceeding and as more water is added, more of the surface is passivated. The corrosion currents generated at the reamining active areas become progressively more intense and lead to the nucleation of a site susceptible to stress-corrosion cracking.

The experimental evidence presented here suggests that Cl^- plays a necessary part in the mechanism since the minimum in the time to failure curves tended to disappear as the NaCl content was decreased. It is assumed, therefore, that the corrosive action of Cl^- and perhaps other halogen ions are associated with the susceptible sites for the nucleation of a stress-corrosion crack.

FIGURE 1. VIEW OF STRESS-CORROSION TESTING APPARATUS SHOWING PARTIAL IMMERSION SETUP (left), A CRACKED SPECIMEN WITH BOTTLE REMOVED (center), AND A STAGNANT IMMERSION TEST IN PROGRESS (right).

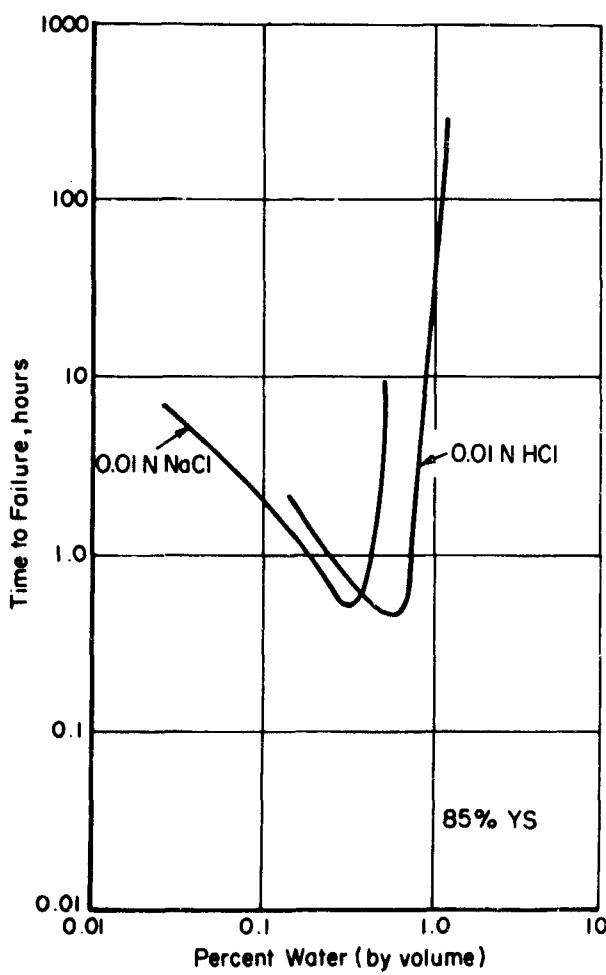
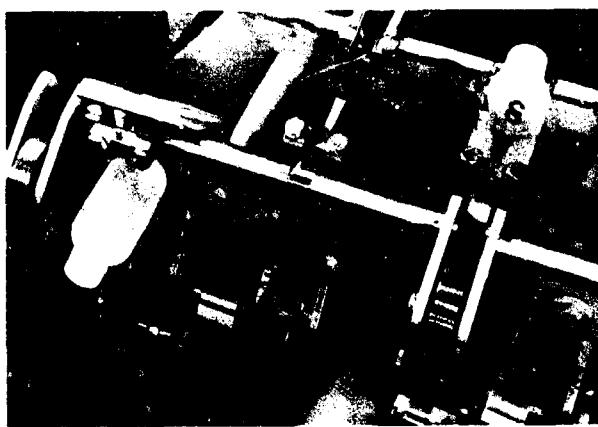


FIGURE 2. EFFECTS OF ADDITIONS OF 0.01N NaCl and 0.01N HCl TO METHANOL

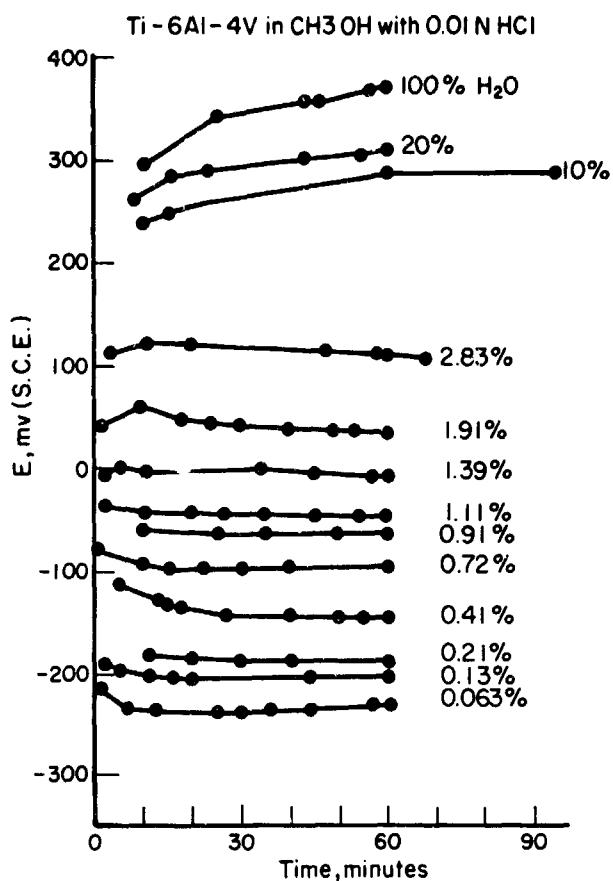


FIGURE 3. EFFECT OF WATER CONCENTRATION ON ELECTRODE POTENTIAL

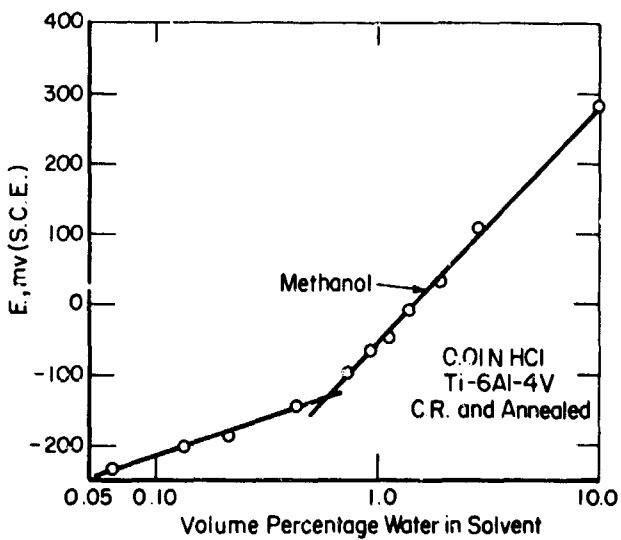


FIGURE 4. EFFECT OF WATER CONCENTRATION ON ELECTRODE POTENTIAL AFTER ONE HOUR

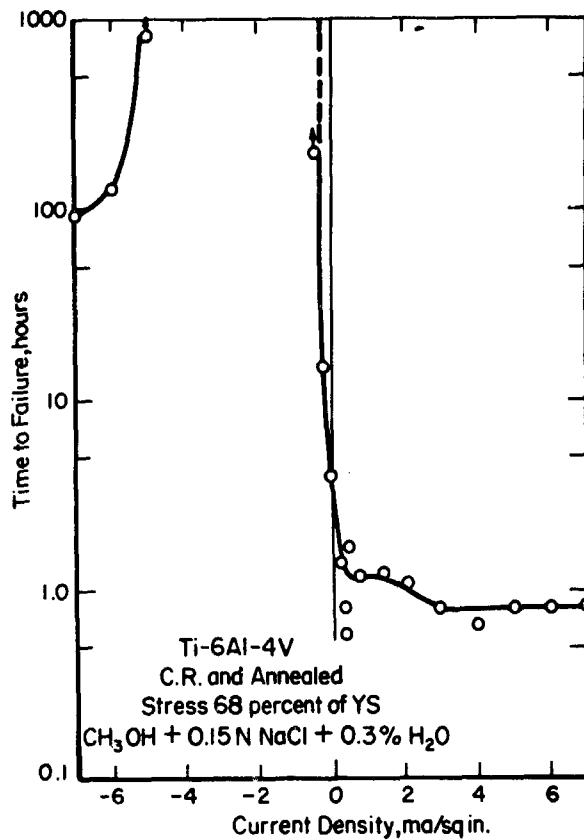


FIGURE 5. SUMMARY OF DATA FOR Ti-6Al-4V ALLOY

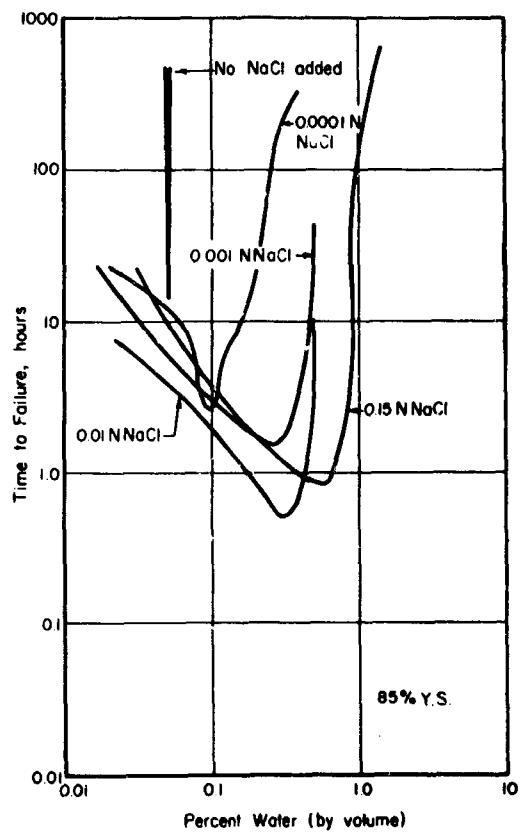


FIGURE 6. EFFECT OF NaCl CONCENTRATION

**RESULTS OF SOME Ti-6Al-4V - METHANOL
EXPERIMENTS AT CONVAIR**

by

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San Diego, California

I would like to remark briefly on a few experiments that we performed using both mill-annealed and solution-treated-and-aged (STA) Ti-6Al-4V. Both notched and unnotched tensile specimens as well as U-bend samples were used.

Our samples were heat-treated separately at a thickness of about 0.125 inch, machined all over and carefully cleaned, and handled with gloves to avoid subsequent staining. Anhydrous methanol was added by fitting a Teflon^(a) sleeve around the test specimen and adhesively binding it to the two shanks at either end of the specimen so that the reduced section was completely immersed in the methanol which was added by means of a hypodermic syringe. We then plugged the hole in the sleeve to insure against moisture absorption during the 10 to 22-day tests.

With chloride-free anhydrous methyl alcohol we obtained no failures on STA Ti-6Al-4V standard sized flat tensile test samples even though some were notched (K_t of 6.3) and subjected to high stresses for long times. Specifically, these samples were subjected to step loading and survived 22 days of stress exposure, the last 10 of which were at 135 ksi, a stress equivalent to 92 percent of the yield stress (147 ksi).

The U-bend specimens were approximately 0.20 x 1/4 x 2 inches and were tested in glass beakers that were also covered with a plastic film to avoid moisture absorption. In this series of experiments, we added various concentrations of hydrochloric acid to the methanol in the beakers. The solutions of hydrochloric acid were prepared by mixing concentrated hydrochloric acid with methanol and successively diluting this solution to parts per million concentrations.

With HCl added to the methanol we obtained failures in the STA Ti-6Al-4V U-bend test specimens at chloride concentrations from 0.5 to 500 ppm in less than 24 hours, and no failure in 109 days in methanol plus HCl at a concentration of 0.05 ppm. With 50 percent by volume of Freon TF added to the methanol, no failure occurred in 109 days. Similarly, no failures have occurred in this time with the bend specimens immersed in an aqueous solution of 500 ppm HCl. While the stresses in the U-bend specimens were not precisely known, the yield strength of the material was exceeded since some slight plastic deformation occurred when they were bent into the U shape for insertion into their slotted holders.

Our feeling regarding the mechanism of cracking and the role played by methanol is as follows:

- (1) The methanol prevents healing the breaks in the protective oxide film when the material is stressed.
- (2) Methanol reacts in some fashion with freshly exposed titanium and residual chloride to form $TiCl_4$ and possibly titanium alcoholates, with the reaction becoming cyclical and self-sustaining and leading to eventual failure.

(a) "Teflon" is a trade name of E. I. DuPont de Nemours & Company, Inc.

DISCUSSION AND SUMMARY

Walter K. Boyd

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I think that there are several points brought out in today's meeting worth reviewing. First of all, it would appear that there is a general need to recognize several types of testing before we can be sure we have the complete answer. Certainly, fracture mechanics play an important role in our testing for stress-corrosion cracking and so does the environment. We can't limit all our studies to classical chemistry on one side and fracture mechanics on the other. I think that we have to be prepared to use a number of types of samples to study the phenomena of both initiation and of crack propagation. Secondly, we have discussed and bandied around here today the role of hydrogen, the role of aluminum, the role of the chloride ion, and of atomic species of chlorine. Certainly not a lot has been said about the role of the stress other than the fact that there is a threshold stress level, below which cracking does not occur. We also have examined a little bit about the role of water in the reaction. For example, we have noted that water is an inhibitor.

Let us consider the data that have been presented today to see where relationships exists. Mr. Johnson has presented evidence that the cracking mechanism is electrochemical in nature since he could stop cracking by applying a cathodic current and obtaining cathodic polarization. By the same token, anodic polarization caused an increase in the rate of attack. This is indeed what one would expect in the case of an electrochemical mechanism. I think it is important for us to realize that there is the possibility of an electrochemical mechanism. If this is the case, then we are dealing with surface reactions and not classical chemistry and possibly not too much about the metallurgy of the system other than how it effects what is adsorbed on the surface and how the surface reaction occurs. The fact that methanol is not exactly an electrolyte isn't of concern since we do have some water present which can act as the electrolyte.

Let's explore for a moment the role of metallurgical structure as it pertains to aluminum and oxygen, particularly in titanium alloys. You have been told here today that there are some indications that the higher the aluminum content, the greater the susceptibility to cracking. The cracking times decreased as the aluminum content was increased. I think that this is an important consideration, particularly in light of the RIAS work. The types of films that are formed on the high aluminum alloy are much less passive than they are on some of the other alloys. It would also appear that oxygen may perform in the same way as aluminum. You will remember that one speaker this morning pointed out that when he took an as-received or machined piece of titanium and heated it four hours in air at 1000 F he found an increase in susceptibility to cracking. He thought this could be due

to surface roughness, but it could also be due to the oxygen pickup. TMCA probably has found that the pitting potentials are radically changed by the oxygen levels, and that as you contaminate the surface with oxygen, the tendency is for more pitting to occur. Thus, we have a more active surface, both with aluminum and with oxygen additions. One must also consider the interaction between aluminum and oxygen when we are talking about increasing susceptibility to crack initiation and propagation.

The role of hydrogen has been suggested as being twofold. Certainly there is some reason to suspect a hydrogen embrittlement mechanism. This is certainly a possibility in methanol vapor. However, in the electrolyte, I believe that the role of hydrogen may be somewhat different. Let us consider the fact that hydrogen is generated at the cathode and that it diffuses into the metal, causing embrittlement. Then, one would also expect a similar situation in the case of cathodic protection. This, however, is not the case. Cracking is stopped by cathodic protection, which suggests that the role of hydrogen is something different than embrittlement. One explanation for this is that maybe the formation of the atomic hydrogen at the surface and in the cathode area would help to reduce any passive films formed on the titanium surface, and thus to maintain an active site at all times. There is some indication that this may be the case since when one applies cathodic protection and then takes it off, cracking takes place almost immediately.

I would suggest the possibility of a third mechanism; that is, that the adsorption of hydrogen on the surface may provide a more active material or phase which corrodes more rapidly than the titanium itself.

Let us now consider the role of water. It is interesting to note that all the cracking of titanium takes place in oxidizing solutions, where titanium is normally quite passive. N_2O_4 is a strong oxidizer. While methanol is not a strong oxidizer by any means, water is present and can act as an oxidizer. Under these conditions one might consider that water acts like an anodic inhibitor, in much the same manner as the chromate ion. We know that chromate certainly passivates the surface of a material. However, if sufficient amounts of an anodic inhibitor are not present, then we get rapid pitting. There is evidence for a critical water level. The data suggest that there is a low point in the water curve in which we don't get any inhibition, and that we get more localized attack as we add small amounts of water. At higher water levels, we passivate or inhibit the reaction. If water acts as an anodic inhibitor and is absorbed preferentially or acts to cut down the number of active anode sites on the surface, then all we do is to concentrate the corrosion in a few of

them, so our attack is pitting or cracking. Now, if we have sufficient water present, the whole surface becomes passivated and no attack takes place.

I think there is a good case to say that the chloride ion may play a special role and that it is probably not the only one. It is true that most chlorides are highly soluble so that we can find a trace of chloride ion in most environments. There have been experiments performed and discussed here today involving an activated chloride ion species. Since the results were inconclusive, one might say that the chloride ion was not particularly necessary to the cracking mechanism. However, there is certainly every indication that the chloride ion will help to obtain film breakdown and maintain an active site. I don't think, however, that chloride ion is the only one and I think that its role here is overemphasized to some extent. I think it will help to promote more rapid failures.

The role of stress in the cracking mechanism is such that it would appear to me that we have to have sufficient stress levels in order to get enough slip to maintain an active site, and to maintain a proper ratio of active metal to the amount of inhibitor that might be present. When one lowers the stress to a certain critical stress level we don't find cracking. I think at this point we do not have sufficient deformation or slip to produce active sites. The surface passivates readily and passivation is maintained.

Last of all, I would like to point out that titanium is not the only material which suffers from stress corrosion cracking. Titanium is an active material, but, so are aluminum, magnesium, and stainless steels. All of these materials depend on the formation of a film on the surface for their passivation. Anything that interferes with this film on the surface will give us an active condition. We've worked with stainless steels and aluminum alloys for many years. I say to you let us learn to design, around titanium's shortcomings but let's not forget that we still have a lot more work to do before we understand the mechanism of cracking.

DISCUSSION

Dr. Roger Staehle - Ohio State University

I'd like to illuminate one point which I think a number of gentlemen have touched on today. The question is what is the role of stress in the process of cracking? Some comment has been made that the presence of stress is something having to do with the internal energy of the systems. In fact, if you make the calculation you find that the change in internal energy is virtually negligible for the stresses in the range that we are interested in. Even in the high stress region of dislocation I expect the stress is relatively small. So it forces us to look for another process that might activate out chemical reaction. What I would like to do is just describe what this process might be and how we might interpret the subsequent reaction. We start out with a clean surface, a schematically clean surface, with an oxide on it and we assume that we have an active

slip plane beneath the oxide film. The presence of stress when sufficiently great will cause slip to occur in that surface, breaking the oxide film. So at some time, say t_0 , we expose unprotected titanium at a relatively low stress. You see you can have a dislocation emergence at a stress quite below the yield which depends on the property of the oxide film. Thus, we can expose this relatively reactive titanium to whatever the environment happens to be, so the next question is what is the course of the reaction from there on.

I'd like to suggest that we might give some thought to an analysis which follows. We think of the reactivity of this slip in terms of a reaction current, J , which is milliamperes per square centimeter versus time, and, with the exposure of the slip step, we have an initial current which drops off. For schematic purposes, we will describe this curve as being $J = J_0 e^{-\frac{t}{T}}$. T is some kind of constant, and t is time. Now you see we have a whole range of reaction processes which occur. A very quick passivation, some intermediate, a higher rate and then a hardly stifled reaction at all. For convenience, let me call this Type 1, Type 2, Type 3, and Type 4. Now, if we are interested in the total amount of reaction that occurs with slip steps, we might very simply say the mass of reaction per event would be the integral of this $J_0 e^{-\frac{t}{T}}$ times the area, which will be a function of time, times the differential of time from times, $t = 0$ to some time when we have complete passivation, say, t_p . We thus get the total amount of reaction that occurs in a given slip step event. You see there are two very important quantities here, one is the passivation constant and the other is the initial reaction current.

Now, it has often occurred to me in discussions here that a particularly fruitful way of analyzing our problem might be to conduct experiments in which we evaluated the rate in which a new formed surface would passivate. Because you see, a surface that passivates very quickly sustains a very small amount of reaction, so that the reaction, for, say, Type 1, would be where virtually no reaction occurred at all, but Type 2 might get a little bit more reaction, and for Type 3 a little bit more. For Type 4, there would probably be a general dissolution and not really any localized attack.

For Type 1 reactions, passivation occurs quickly, and it's going to be very difficult to initiate and propagate a reaction. This might correspond to certain environments which are highly passivating and we don't get cracking. Now, Type 2 might correspond to the case where, once we got a significant flux of slip steps, we could sustain a continued generation of this local dissolution and would progress a crack. Here, we would have difficulty initiating a crack but propagation would be easy. This would be a case for titanium in salt water when you have to put in a prior fatigue crack.

Now the third case would be for this less easily passivated case. It would be easy to initiate something because the amount of initial dissolution is great and also easy to propagate, and this

would apply to the general N_2O_4 system and, perhaps, also to the methanol group that we are talking about, because in many cases both systems are self-propagators. And finally, the question of Type 4 will be something that is a relatively heavy corrosion process, so this would just be extensive corrosion. This might provide us a way of looking (1) at the role of stress and (2) give us a parameter by which we can assess the role of specific environment-alloy combinations.

Using this general idea, several possibilities for protection are obvious. For example, one method of protection would be to emphasize adding elements which would give you a ready passivation, like the nitrate someone mentioned, or perhaps the chlorate. Other possibilities for experiments are use of thin foils. Expose them to your environment in the stressed condition, take them out and look at them to see where the preferential reaction was occurring and see if it was occurring where we have a moving dislocation. We might also expose a bulk sample in the environment, stress it and see if you have an excessive amount of reaction product formed at the slip step. Finally, you might use the old experiment of a straining wire and measure current density at a given potential. Then measure the decay rate when you stopped the straining and the decay rate would be approximately indicative of your value T . There is an abundance of experimental evidence for the slip step activity and for this general kind of analysis if any of you care to pursue it.

Q: How do you rationalize the fact that shot-peening protects it in terms of corrosive chemical activity?

A: Staehle. Well, because the shot-peening prevents the emergence of actual slip planes.

Boyd. I fully agree. It lowers the tensile stress level on the surface.

Q: Is the oxide you form on the surface different from the condition prior to the time you stressed it?

A: Boyd. No, I don't think the oxide is different. The only thing about it is when you shot-peen, it raises the threshold level at which you are going to have to go in order to get slip to take place, since you are putting compressive stress on the surface, not tensile stresses.

Ken Weber - Lockheed, California

We became interested in this problem of stressed wires so we built an experimental apparatus to take a look at the potentials involved here. We have a ring about six inches in diameter with a setup so we can loop a piece of titanium wire over it. Down at the lower end, we put weights up to 300 or 400 pounds on the end of the wire. The wire came directly through the flask, in which we could put any corrodent we want. We covered all the wire except a very small area so we could observe what was happening. We measured the potential with respect to a calomel electrode with the salt bridge between the titanium and the salt water.

Without load we got some potential with respect to the calomel electrode and it was fairly stable. Now as soon as we loaded the wires, we got a tremendous activation as you might expect in the potential. It went very negative, then it passivated rather rapidly in 5 percent salt water. The interesting thing here is that this kept occurring over and over again. Every once in awhile another peak would show up as long as it was under stress, although they got farther and farther apart. When we reloaded the wire, we no longer got this large peak but it was more characteristic of the smaller peak. This is pretty good evidence that this slip does occur and doesn't only occur on the initial loading. It keeps occurring uniformly over the surface.

Boyd. I certainly agree with this. We have done some quite similar work with titanium and we find that at a stress level, all of a sudden we don't see any of these steps. The potential goes very negative and stays that way.

Q: Johnson and Haney both talked about polarization preventing the stress cracking. Were they able to arrest a crack that was already started, like cathodic polarization?

Boyd. I don't know if anyone has arrested a crack in methanol that was already started but it certainly has been done in seawater. Would anybody like to comment if they have done this type of study in methanol?

Howard Herrigel - Boeing. I personally haven't done any of this work but Dr. Ted Beck, working at Boeing Scientific Research Laboratory, has been investigating the electrochemistry corrosion of titanium and he is recently working with cracked specimens. He tells me that he has been able to arrest cracks in methanol solutions with some additions which I don't recall. But he has been able to arrest these cracks by application of cathodic potentials.

Q: Joe Ryniewicz - Lockheed MSC. There was a chart given earlier this morning on flaw size but is there any information on flaw size indicating what is permissible with N_2O_4 ? Is there a size which will not propagate?

Boyd. I think it would be very difficult to say that there is a size that will not propagate. It will again depend upon the stress loads that are applied and the shape of the flaw.

Q: Grant Rowe-Battelle-Northwest. On your comment that water accelerated cracking faster than the alcohols methanol or ethanol, we haven't found this in our testing. We find that ethanol on the steel is a good order of magnitude greater than water at stress levels that I had in my graph.

Boyd. I am just referring to what Rostoker's data showed. This has been duplicated by other people, and the Russians report about the same type of information. It depends upon a number of factors.

Herman Wisenberg - American Oil Company

Your comment that titanium is not the only thing by a long shot that cracks in methanol is true. In the course of laboratory investigations, we tried a few other metals. Zirconium will also stress crack.

Jim Jackson - Battelle-Columbus

The article by Mori that we have been quoting, I believe, also reports some work with zirconium.

Q: Most of the information on testing seems to be under conditions where you have loaded the test specimen in either a U-bend or the pre-cracked test. In either case it is under continuous exposure to the so-called contaminated element, methanol. Has there ever been any information from the test to show what the delay might be from the exposure and then re-loading at a later date?

Boyd. I really don't know of any. I would throw that question open to anyone on the floor. Does anybody care to comment on this?

Anonymous - I may add something else to that - In my experience up to now with failures with titanium exposed to methanol and possibly Freons or halogenated hydrocarbons - there have been incidents where they have been exposed to this material and have not failed at that time, but have at a later date.

Boyd. I can certainly see where one could get some initiation of cracks that were not sufficient enough to cause failure at that time and then upon a subsequent exposure, would be right for propagation again at a known stress eventually leading to failure.

Q: Would you care to elaborate on that applied to Freon?

Anonymous Reply. Only in regards that Freon was one of the elements with methanol that was present. In other words, it was exposed to those two compounds. At a later date, one of the specimens that had been exposed under stress was then cleaned out and purged, and then was retested to failure at a lower stress than expected.

Howard Herrigel - Let me point out that there is another practical consideration concerned with the exposure to methanol. In any large-scale fabrication program, at least in a commercial vehicle, unless you are aware of the fact that there is going to be a problem, you're probably going to be exposed to methanol whether you know it or not. Methanol occurs in paint stripper, marking ink, solvents and a million places in the shop, and it also occurs in deicing fluids whether you like it or not. You better make sure you track these things down to get rid of them or else know what the effects are.

Q: Keller, NASA. Would anyone care to comment on the advisability of removing heat treating stain or discoloration for titanium?

Howard Herrigel - Boeing - I have done this test - and of course as the tank failure showed, with the blue oxide coating on it, it is more susceptible to crack initiation. We might be forgetting that there are probably considerable defect sites available in this colored oxide layer and chemical reactions can initiate at these sites, also. Certainly my data show that you can have cracking in half the time if you have the heat-treat-discolored layer on the specimen.

Q: What can be done to avoid or reduce stress-corrosion cracking in titanium?

Boyd. There are several things that might be done. One is to get the tensile stress on the surface. I would say that you must inhibit some of these environments, and we know something about the inhibitors. So if we have to use these environments, then we must use an inhibited condition to minimize chances and to get it cleaned out thoroughly thereafter so we don't get below these conditions that will give us passivation.

Anonymous: I want to make a comment here which you have to keep in mind, I think. A lot of this work is being done with specimens which contain fatigue cracks which are very critical notches and we're attempting to simulate the type of flaws or surface cracks which will occur in structure either from an inherent metallurgical or geometric discontinuity. We not only then have to talk about what we can do to the titanium in a chemical sense, but we have to talk about what we can do to screen for defect sizes which we can inspect out. Now, this is the same type problem we've been fighting with aluminum for a period of years, and the inspection techniques which we've utilized in dealing with aluminum have saved us with regard to this problem. I certainly agree with Boyd very highly - good housekeeping and inspection are things that always help us to have a high competence level in material that we have.

Boyd. Hopefully a meeting of this type and continued discussions will get the information out to the people who are doing the work. Make them understand how serious the need is for good quality control and housekeeping procedures in order for us to get high-integrity material. I know it is hard for some of them to believe, but when we start using materials near the ultimate in properties, then the reaction of the environment become so very important. Look at our bridges of hard iron. These rust, so we paint them and we go about our business. But when we go to higher and higher strength materials then we cannot have this lack of knowing what we have, we just have to do a better job. I think the trend is to get better housekeeping and it will continue.

Anonymous. I would like to add only one thing further. I am sure that if we can utilize in our present structures the very high-strength steels that we do use (as susceptible as they are to hydrogen embrittlement) and do it at least relatively successfully, we can certainly learn and institute the procedures that we need to use titanium satisfactorily.

APPENDIX A

**INVESTIGATION OF STRESS CORROSION OF ELECTRON BEAM WELDED
AND NONWELDED Ti-6Al-4V IN SOLUTIONS OF METHANOL AND
ISOPROPYL ALCOHOL AT ROOM TEMPERATURE**

This paper was submitted to DMIC after the seminar
and is included in this memorandum for purposes of record.

**INVESTIGATION OF STRESS CORROSION OF ELECTRON-BEAM-WELDED AND NONWELDED
Ti-6Al-4V IN SOLUTIONS OF METHANOL AND ISOPROPYL ALCOHOL AT ROOM TEMPERATURE**

by

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INTRODUCTION

Marquardt has several applications which utilize titanium alloys for propellant storage tanks in various rocket engines. These components and associated hardware presently require the use of pressurized alcohol for flushing and decontamination of the system. A preliminary evaluation was initiated to investigate the phenomenon of titanium alloy stress corrosion in methanol as a result of the recently reported Apollo tank failure. Transverse and longitudinal samples of ELI grade Ti-6Al-4V, solution treated and aged to average ultimate strengths of 155,300 psi and 151,900 psi, respectively, were exposed to solutions of methanol and isopropyl alcohol at stress levels of 77,000 psi (approximately 50 percent of the ultimate strength). Electron-beam-welded specimens in the annealed condition were also included in the evaluation at a stress level of 50,000 psi.

CONCLUSIONS

- A. Solution-treated-and-aged (155,300-psi ultimate strength) Ti-6Al-4V is susceptible to rapid (less than 3 days) stress-corrosion failure in anhydrous methanol at room temperature when stressed to 50 percent of the ultimate strength.
- B. The addition of 1 percent distilled water to the anhydrous methanol prevented the stress corrosion of identical specimens (as described in A above) during test durations of up to 35 days. However, these same specimens failed in less than 4 days when exposed to anhydrous methanol.
- C. Electron-beam-welded Ti-6Al-4V samples in the annealed condition did not exhibit any indications of stress corrosion during 28-day room-temperature tests at stress levels of 50,000 psi when immersed in (a) anhydrous isopropyl alcohol, (b) anhydrous isopropyl alcohol plus 1 percent distilled water, or (c) an isopropyl alcohol base dye penetrant developer solution (Turco Dy-Chek Developer). Two of these samples were reexposed in anhydrous methanol with stress-corrosion failures occurring in the parent metal in less than 4 days and 11 days, respectively.

PROCEDURE

Specimen Preparation

Two different lots of ELI grade Ti-6Al-4V were used in this evaluation. The nonwelded transverse and longitudinal specimens were fabricated from 0.375-inch-thick plate procured to AMS 4911 in the annealed condition from Titanium Metals Corporation of America, Heat No. G1363. The plate was solution heat treated at 1750 F for 1 hour in air and quenched to below 1100 F in less than 8 seconds. After machining to final size (3.0 x 0.5 x 0.040 inch), the specimens were vacuum aged for 8 hours at 1110 F. These specimens had previously been exposed for 30 days at a 45,000-psi stress level in green nitrogen tetroxide (N_2O_4) plus 0.60 ± 0.20 percent NO at 120 F. The nitric oxide content at the start of the test was 0.45 percent. These samples were from a program which has subsequently accumulated an additional exposure of 5 months at room temperature with no failures. Typical specimens with the same exposure as those used in this evaluation have been examined metallographically for indications of intergranular attack and by mechanical testing to determine any loss of mechanical properties. No degradation was observed.

Butt weld tabs (1.5 x 0.5 x 0.073 inch) were machined from 0.125-inch-thick Ti-6Al-4V sheet procured to MIL-T-9046E, Type 3, Comp. D, in the annealed condition from Titanium Metals Corporation of America, Heat No. G-784. The test specimens were butt welded by the electron-beam process in accordance with Marquardt's Materials Process Specification 1609. The specimens (3.0 x 0.5 x 0.073 inch) were exposed in the as-welded condition without subsequent machining.

Cleaning Procedure

The specimens were cleaned by immersion for 2 minutes at room temperature in a solution of 50 ounces of nitric acid and 5 ounces of hydrofluoric acid in distilled water to make 1 gallon. The samples were then washed in a mild alkaline solution consisting of 30 percent sodium hydroxide in distilled water for 5 minutes. Prior to bagging, the samples were detergent cleaned by immersion in a solution of 1-1/3 ounces of trisodium phosphate per gallon of distilled water at 120 F and scrubbing with a stiff nylon brush. Each cleaning operation was followed by a cold-and hot-water rinse. The specimens were handled with gloves or tongs after the start of the cleaning cycle.

Stress Application

The tensile stresses were obtained by berding the specimens in a four-point loading fixture (Figure 1). The fixtures were AISI 321 stainless steel with titanium anvils to prevent contact between dissimilar metals, thus avoiding any possible galvanic attack. The ends of the specimens were wrapped with Teflon tape for galvanic protection.

A strain gage was applied to the tension side of each specimen. The desired stress level was established with a Baldwin SR4 strain indicator calibrated in microinches by turning a set screw against the anvil on the compression side of the specimen. A Young's modulus of 16.8×10^6 psi was assumed for the stress relation. The specimens were stressed and allowed to set for a minimum of 72 hours and then rechecked to compensate for any drift or relaxation due to the Teflon insulation. The strain gages were removed with acetone followed by a low-temperature (150 F) bake for 15 minutes in air.

Test Environment

The stressed test specimens were exposed to the following alcohol solutions for up to 35 days at room temperature.

- (1) Anhydrcus methanol containing less than 0.02 percent water.
- (2) Anhydrous methanol with a 1 percent distilled water addition.
- (3) Anhydrous isopropyl alcohol containing less than 0.25 percent water.

- (4) Anhydrous isopropyl alcohol with a 1 percent distilled water addition.

- (5) Isopropyl alcohol base dye penetrant developer solution (Turco Dy-Chek Developer).

Glass ampoules shown in Figure 2 (2 inches in diameter and 8 inches long) were used to hold the specimens and contain the various alcohol solutions during the exposure period. A maximum of two samples were loaded into each ampoule. The open end of the ampoules were sealed with a T321 stainless steel closure and a Teflon "O" ring. The closure plate has a shut-off valve and a connection for attachment to a combination vacuum and filling manifold. The specimens were loaded into the ampoules, which were then pressure checked to avoid loss of the solution or changes in its composition due to a bad seal. The ampoules were evacuated and backfilled with the desired solution. This filling technique was used for all of the ampoules, with the exception of the isopropyl alcohol base dye penetrant developer. The developer solution was poured over the specimens in an ampoule before the closure plate was attached. This ampoule was not pressure checked; however, the liquid level did not change during the 28-day exposure period. The solids in the developer solution had a tendency to settle out of solution and required daily agitation. The ampoules were maintained in an upright position between 70 and 80 F for the duration of the exposure period (see Table 1). The ampoule was visually examined at the start and close of each workday for failures or initiation of cracks.

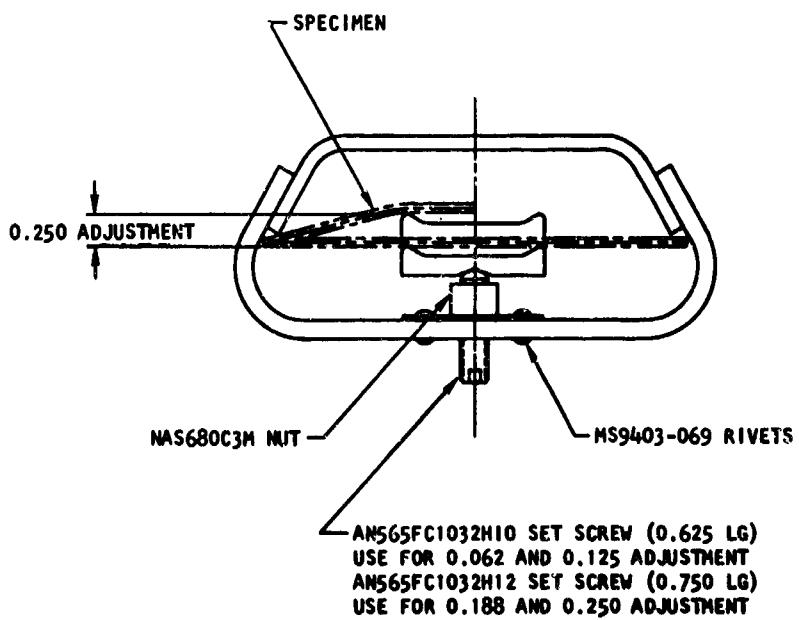


FIGURE 1. TEST-FIXTURE ASSEMBLY.

DISCUSSION OF RESULTS

The results of this limited evaluation are summarized in Table 1. The sheet specimens had been previously exposed to green nitrogen tetroxide (N_2O_4) at a stress level of 45,000 psi for 30 days at 120 F. Post-test evaluations of similarly exposed samples did not reveal any indication of intergranular attack or loss of mechanical properties. Two sets of specimens consisting of a longitudinal and a transverse Ti-6Al-4V specimen per set were stressed to 77,000 psi (50 percent of the ultimate strength) surface tension. The transverse specimen exposed in the anhydrous methanol failed due to stress corrosion attack during a weekend between 4 and 52 hours of exposure. The longitudinal specimen in the same ampoule failed at night between 60 and 74 hours. The two identical specimens immersed in the methanol with a 1 percent distilled water addition were unaffected at the termination of this phase of the test after 35 days of exposure. At the conclusion of the above exposure, the latter two specimens were removed from the distilled-water-inhibited solution and retested at the same stress level in anhydrous methanol. Both specimens failed due to stress corrosion attack during the night between 74 and 89 hours.

The electron-beam-welded Ti-6Al-4V specimens in the annealed condition were exposed to anhydrous isopropyl alcohol, anhydrous isopropyl alcohol with a 1 percent distilled water addition, and an isopropyl alcohol base dye penetrant developer solution (Turco Dy-Chek Developer). The specimens were stressed to a surface tension of 50,000 psi. No failures or indications of stress corrosion were observed after the 28-day exposure. The two samples (Numbers 7 and 8, Table 1) exposed to the water-inhibited isopropyl alcohol were retested in anhydrous methanol at the same stress level. One sample failed during the night between 50 and 65 hours and the second sample failed over a 2-day weekend between 165 and 255 hours. The two electron-beam-welded specimens failed in the parent metal approximately 1/4 inch outside of the heat-affected zone.

The results of this evaluation indicate that both longitudinal and transverse, solution-heat-treated-and-aged Ti-6Al-4V sheet stressed to 77,000 psi (50 percent of the ultimate strength) and electron-beam-welded Ti-6Al-4V in the annealed condition stressed to 50,000 psi are not susceptible to stress-corrosion attack in isopropyl alcohol solutions at room temperature. However, extremely rapid stress-corrosion failures of material in the same condition were observed in anhydrous methanol. The addition of as little as 1 percent distilled water to the anhydrous methanol is sufficient to inhibit stress corrosion for up to 28 days. Due to the limited number of specimens available for this preliminary investigation, the results should only be used to establish trends until additional work has been performed.



FIGURE 2. STRESS-CORROSION SAMPLE AND FIXTURE

TABLE 1. STRESS-CORROSION TEST RESULTS

Specimen	Type Specimens		Direction		Stress Level, psi	Previous Exposure	Test (d) Environment	Test Duration	Remarks
	Sheet (a)	EB Welded (b)	Trans.	Long.					
1	x	x	x		77,000	N ₂ O ₄ + 0.45% NO, 120 F 30 Days (c)	Methanol	4-52 hr	Failed
2	x		x		77,000	N ₂ O ₄ + 0.45% NO, 120 F 30 Days (-)	Methanol	60-74 hr	Failed
3	x				77,000	N ₂ O ₄ + 0.45% NO, 120 F 30 Days (c)	Methanol + 1% H ₂ O	35 days	No change
4	x		x		77,000	N ₂ O ₄ + 0.45% NO, 120 F 30 Days (c)	Methanol + 1% H ₂ O	35 days	No change
5		x	x		50,000	None	Isopropyl	28 days	No change
6		x	x		50,000	None	Isopropyl	28 days	No change
7		x	x		50,000	None	Isopropyl + 1% H ₂ O	28 days	No change
8		x	x		50,000	None	Isopropyl + 1% H ₂ O	28 days	No change
9		x	x		50,000	None	Isopropyl base dye penetrant developer	28 days	No change
10		x	x		50,000	None	Isopropyl base dye penetrant developer	28 days	No change
11	x		x		77,000	Continuation of Spec 3	Methanol	74-89 hr	Failed
12	x		x		77,000	Continuation of Spec 4	Methanol	74-89 hr	Failed
13		x	x		50,000	Continuation of Spec 7	Methanol	50-65 hr	Failed in parent metal
14		x	x		50,000	Continuation of Spec 8	Methanol	165-255 hr	Failed in parent metal

(a) ELI grade Ti-6Al-4V 0.040-inch-thick sheet, solution heat treated and aged to an average longitudinal ultimate strength of 155,300 psi and 151,900 psi in the transverse direction.

(b) ELI grade Ti-6Al-4V 0.073-inch-thick sheet, procured in the annealed condition to a minimum ultimate strength of 130,000 psi.

(c) See text for details.

(d) The specimens were fully immersed for the duration of each test.

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228	Accelerated Crack Propagation of Titanium by Methanol, Halogenated Hydrocarbons, and Other Solutions, March 6, 1967
229	Melting and Casting Review, November 15, 1967

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13. ABSTRACT This memorandum presents transcripts of the papers given at a seminar held at Battelle Memorial Institute in Columbus, Ohio on March 6, 1967. The papers, for the most part, are concerned with experiences of the speakers organizations with stress corrosion cracking of titanium and its alloys by both water solutions and solutions based on organic liquids. A discussion of the possible mechanisms involved is included.		

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